# UNCLASSIFIED

# AD 282 493

*Reproduced*
*by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

# UNCLASSIFIED

282 493

# RADIO CORPORATION OF AMERICA
# RCA LABORATORIES

FINAL REPORT

## ELECTRONIC SPECTRA OF
## TRANSITION METAL IONS IN CRYSTALS

PART II

CONTRACT NO. AF19(604)-5541
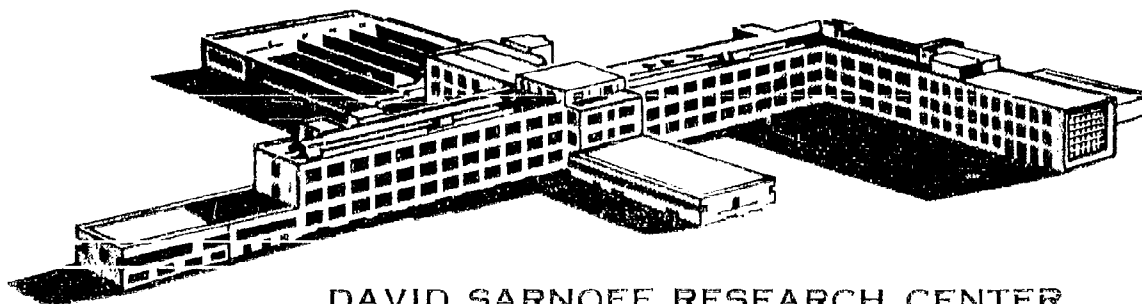
## DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

# ELECTRONIC SPECTRA OF
# TRANSITION METAL IONS IN CRYSTALS

Donald S. McClure, Santiago R. Polo, and Herbert A. Weakliem

RCA LABORATORIES
RADIO CORPORATION OF AMERICA
PRINCETON, NEW JERSEY

PROJECT 5621
TASK 56211

PART II

FINAL REPORT

CONTRACT NO. AF 19(604)-5541

JUNE 1, 1961

Requests for additional copies by Agencies of the Department
of Defense, their contractors, and other Government agencies
should be directed to the:

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

Department of Defense contractors must be established for
ASTIA services or have their "need-to-know" certified by
the cognizant military agency of their project or contract.

All other persons and organizations should apply to the:

U. S. DEPARTMENT OF COMMERCE
OFFICE OF TECHNICAL SERVICES
WASHINGTON 25, D. C.

# STUDIES ON CRYSTAL FIELD THEORY

S. R. POLO

RCA LABORATORIES
PRINCETON, NEW JERSEY

# TABLE OF CONTENTS

*iii*

# TABLE OF CONTENTS (Cont'd)

# 1. COORDINATE TRANSFORMATIONS

Let $x_1$, $x_2$, ..., $x_i$, ..., $x_n$ denote the coordinates of a point in the configuration space of a physical system. To every value of the index $\underline{i}$ there correspond, in general, a set of values of several indices necessary to specify the variable. For example, if the system is composed of several particles, there may be an index indicating the kind of particle, another specifying a particular particle from among several of the same kind; if $x_i$ is a space coordinate another index, which may assume three different values, shall also be described by the symbol $x_i$ , etc.

The values of a scalar physical quantity at the points of the configuration space will be considered, by definition, to be independent of the reference system. In a particular system they may be expressible as a certain function of the coordinates $f(x_1, x_2, ..., x_n)$. If a change of reference system is made such that the point with coordinates $x_1, x_2, ..., x_n$, in the original system has the new coordinates $x_1', x_2', ..., x_n'$, in the new system, the definition implies that the identity

$$f(x_1, x_2, ..., x_n) = f'(x_1', x_2', ..., x_n') \qquad (1\text{-}1)$$

is satisfied at every point of the configuration space.

One may also think of the transformation as rotating the points of the configuration space or the physical system, leaving the reference frame unchanged. In either case, the definition (1-1) expresses the fact that the value of the physical quantity at a physical point is assumed invariant.

In general, the explicit form of the new function $\underline{f'}$ in terms of the variables $x_1'$, $x_2', ..., x_n'$ will be different from that of the original function f in terms of $x_1, x_2, ..., x_n$. If it is the same, the function is said to be symmetric under the transformation in question. The study of the transformation properties of the eigenfunctions of physical systems is a subject of considerable interest.

The coordinate transformations to be considered are rotations of the coordinate axes, inversion at the origin, and permutations of the indices of identical particles. The coordinates of a point in the original system and in the new one are related by a unitary transformation

$$x_i' = \sum_j R_{ij} x_j \qquad (1\text{-}2)$$

If we denote by $x$ a column vector with components $x_1, x_2, \ldots, x_n$, and similarly for $x'$, we may write Eq. (1-2) in matrix notation

$$x' \quad R x \tag{1-3}$$

The transformed function $\underline{f}'$ will be denoted by $Rf$, and we may write Eq. (1-1) in the form

$$f(x) \quad Rf(Rx) \quad SRf(SRx) \tag{1-4}$$

The explicit form of the transformed function can be determined from the form of $f(x)$ and the transformation matrix $R$, by expressing $x$ in terms of $x'$

$$Rf(x') \quad f(R^{-1}x') \tag{1-5}$$

The right-hand side may then be expressed in terms of an orthonormal set of basis functions in the same variables, $x'$. The primes may then be omitted so that one arrives at an expression of the form

$$Rf(x) = \sum_i f_i(x) \, (f_i | Rf) \tag{1-6}$$

where the coefficients depend only on the parameters characterising the transformation.

The transformation may be considered as an operator acting on functions to generate other functions. The definition by means of an equation of the form (1-6) is consistent with Eq. (1-1) when the right-hand side is interpreted as in Eq. (1-5).

It is perhaps worthwhile to illustrate the meaning of Eq. (1-6) by considering the case when the function $f(x)$ is one of the coordinates themselves. In order to avoid confusion we shall write

$$f_i(x) \quad x_i(x) \quad x_i \tag{1-7}$$

Eq. (1-5) is now

$$Rx_i(x') \quad x_i(R^{-1}x') \quad \sum_j (R^{-1})_{ij} x'_j \tag{1-8}$$

If we now omit the primes, we obtain an expression in the form of Eq (1-6)

$$Rx_i(x) = \sum_j (R^{-1})_{ij} x_j \tag{1-9}$$

This is not merely the inverse relation of Eq. (1-2) relabelled, since the definition (1-1) is implicit in the form of writing the left-hand side. We shall see the difference more clearly

when we consider the definitions, not equivalent to Eq. (1-1), adopted by other authors. One should also notice that with the present definition we cannot identify $x_i'$ with the transformed function of $x_i$.

The previous definition of the transformed function is adopted by Wigner[1] and Edmonds[2] but it is not the only one followed, and care should be exercised when comparing or making use of results and expressions in the literature. Some authors[3] define the transformed function as the original function of the new coordinates

$$f(x') = R f(x) = f(Rx) \tag{1-10}$$

and therefore

$$SR f(x) = f(SR x) \tag{1-11}$$

For the inverse transformation

$$R^{-1} f(x) = f(R^{-1}x) \tag{1-12}$$

This expression should be compared with Eq. (1-5). It may be seen that for a given function $\underline{f}$ and a given transformation matrix $R$, the right-hand side in both equations is the same (the primes may be omitted). However, while Eq. (1-5) defines the corresponding operator as $R$, the operator defined by Eq. (1-12) is the inverse, $R^{-1}$.

As before, we may consider the case when the original function is one of the coordinates. According to Eq. (1-10), we have now in place of Eq. (1-8)

$$R x_i(x) = f_i(x') = x_i' \tag{1-13}$$

so that, according to this definition, the transform of one of the coordinates is the corresponding coordinate in the new reference system. In place of Eq. (1-9) we now have

$$R x_i(x) = \sum_j R_{ij} x_j \tag{1-14}$$

It may be seen that the matrices whose elements are the coefficients appearing on the right-hand sides of Eqs. (1-9) and (1-14) are inverse to each other.

It is convenient to point out the differences that these two definitions introduce in the expressions for the transformation of the angular momentum eigenfunctions under rotations. These are usually written in the form

$$R(\alpha\beta\gamma)|jm\rangle = \sum_{m'} |jm'\rangle D_{m'm}^{(j)}(\alpha\beta\gamma) \tag{1-15}$$

Wigner[1] and Edmonds[2] adopt the definition corresponding to Eq. (1-4) while Rose[3] and others follow the one corresponding to Eq. (1-10). For a given rotation characterized by three Eulerian angles defined and labelled in identical fashion, the coefficients $D_{mm'}^{(j)}(\alpha\beta\gamma)$ in their corresponding expressions are the elements of matrices $\mathbf{D}^{(j)}(\alpha\beta\gamma)$ which are the inverse of each other, so that

$$D_{mm'}^{(j)}(\alpha\beta\gamma)_{\text{Wigner}} = D_{m'm}^{(j)}(\alpha\beta\gamma)^*_{\text{Rose}} \tag{1-16}$$

Although their expressions do not appear at first sight to satisfy this relation, this is only due to the fact that the three Eulerian angles are designated by Wigner as $\gamma$, $\beta$, and $\alpha$, while the same angles are designated as $\alpha$, $\beta$, and $\gamma$ by Rose.

Edmonds[2] follows the same definitions as Wigner and his expression for the $D_{mm'}^{(j)}(\alpha\beta\gamma)$ is also the same. However, his designation of the above Eulerian angles is $\alpha$, $\beta$, and $\gamma$ and this is inconsistent with the definitions adopted. His expressions are valid only if the labels $\alpha$ and $\gamma$ are interchanged either in his definition of the Eulerian angles or in the expressions for the elements $D_{m'm}^{(j)}(\alpha\beta\gamma)$ and those derived from it. This may be easily seen if one considers that the operator $R(\alpha\beta\gamma)$, defined as the product

$$R(\alpha\beta\gamma) = R_z(\alpha)\, R_y(\beta)\, R_z(\gamma) \tag{1-17}$$

corresponds, according to Eq. (1-4), to the product of three coordinate transformations

$$\mathbf{x}' = \mathbf{R}_z(\gamma)\, \mathbf{x}$$
$$\mathbf{x}'' = \mathbf{R}_y(\beta)\, \mathbf{x}' \tag{1-18}$$
$$\mathbf{x}''' = \mathbf{R}_{z''}(\alpha)\, \mathbf{x}''$$

or

$$\mathbf{x}''' = [\mathbf{R}_{z''}(\alpha)\, \mathbf{R}_{y'}(\beta)\, \mathbf{R}_z(\gamma)]\, \mathbf{x}$$

the first one being a rotation by an angle $\gamma$ about the original z-axis, and the last one a rotation by $\alpha$ about the intermediate z''-axis.

## EXAMPLES

We shall illustrate the transformation of the spherical harmonics $Y_\ell^m(\theta,\phi)$ under some of the simplest coordinate transformations. The definition and some of the most pertinent properties of the spherical harmonics are given in Appendix A.

$\underline{R_z(\alpha)}$. Rotation of the coordinate frame about the z-axis by an angle $\alpha$.

The expressions for the original polar angles of a point P in terms of the new ones are (see Fig. 1-1)

$$\theta = \theta'$$
$$\phi = \phi' + \alpha$$

Since

$$e^{im(\phi' + \alpha)} = e^{im\alpha} \cdot e^{im\phi'}$$

it follows that

$$R_z(\alpha) \, Y_\ell^m \, (\theta', \phi') = Y_\ell^m (\theta', \phi' + \alpha) = e^{im\alpha} \, Y_\ell^m (\theta', \phi')$$

We can now omit the primes.

$$R_z(\alpha) \, Y_\ell^m (\theta, \phi) = e^{im\alpha} \, Y_\ell^m (\theta, \phi)$$

We shall even omit the polar angles, for simplicity, and write

$$R_z(\alpha) \, Y_\ell^m = e^{im\alpha} \, Y_\ell^m . \tag{1-19}$$

$\underline{R_x(\pi)}$. Rotation about the x-axis by an angle $\pi$. (See Fig. 1-2)

$$\theta = \pi - \theta'$$
$$\phi = 2\pi - \phi'$$

Since

$$\Theta_\ell^m (-\cos\theta') = (-1)^{\ell + m} \Theta_\ell^m (\cos\theta') = (-1)^\ell \Theta_\ell^{-m}(\cos\theta')$$

and

$$e^{im(2\pi - \phi')} = e^{-im\phi'}$$

it follows that

$$R_x(\pi) \, Y_\ell^m = (-1)^\ell \, Y_\ell^{-m} \tag{1-20}$$
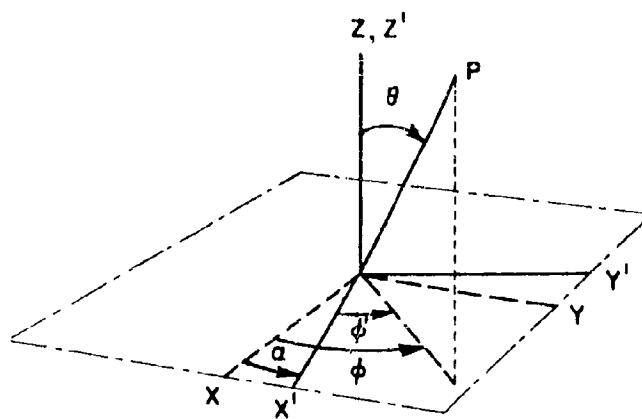
FIG. 1-1  $R_z(\alpha)$
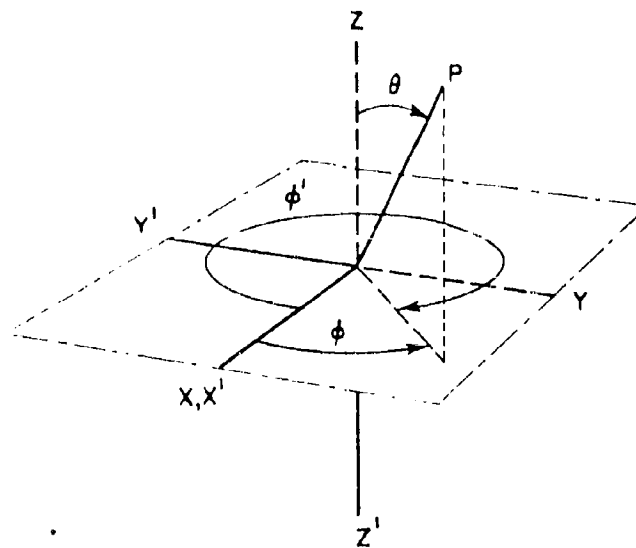
FIG. 1-2  $R_x(\pi)$

$\underline{R_y(\pi)}$. Rotation about the y-axis by $\pi$. (See Fig. 1-3)

$$\theta = \pi - \theta'$$
$$\phi = \pi - \phi'$$

Since

$$\Theta_\ell^m(-\cos\theta') = (-1)^\ell \Theta_\ell^{-m}(\cos\theta')$$

and

$$e^{im(\pi-\phi')} = (-1)^m e^{-im\phi'} \qquad (1\text{-}21)$$

we finally have

$$R_y(\pi)\, Y_\ell^m = (-1)^{\ell+m}\, Y_\ell^{-m}$$

*INVERSION*

Inversion through the origin (Fig. 1-4)

$$\theta = \pi - \theta'$$
$$\phi = \phi' - \pi$$

Since

$$\Theta_\ell^m(-\cos\theta') = (-1)^{\ell+m} \Theta_\ell^m(\cos\theta')$$

and

$$e^{im(\phi'-\pi)} = (-1)^{-m}\, e^{im\phi'}$$

we finally obtain

$$I\, Y_\ell^m = (-1)^\ell\, Y_\ell^m \qquad (1\text{-}22)$$
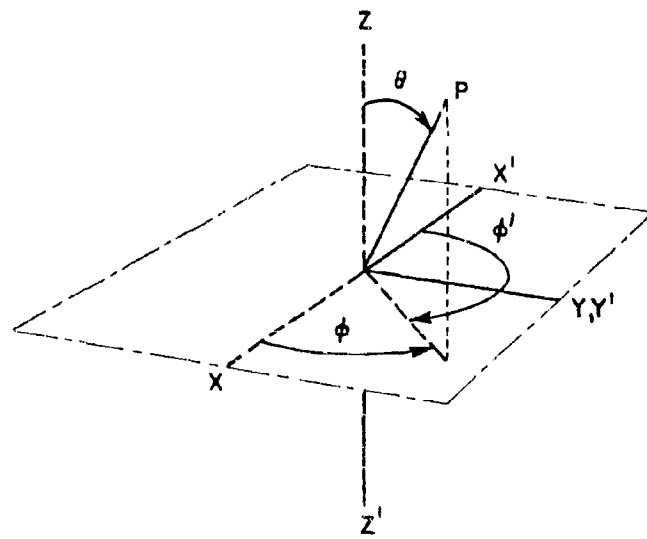
FIG. 1-3   $R_Y(\pi)$
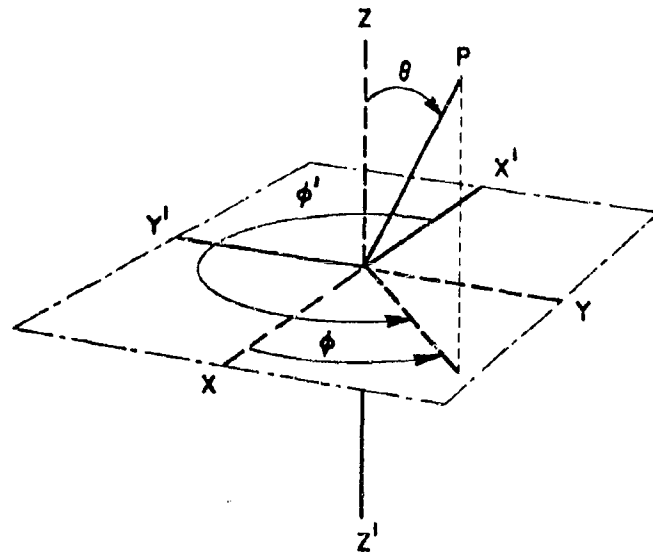


FIG. 1-4   $I$

# 2. BASIS FUNCTIONS, OPERATORS.

In what follows we shall use Dirac's notation whenever convenient (*). Functions shall be labelled by one or several indices or quantum numbers, and written in the form

$$|\psi_{\alpha\beta\gamma...}) = |\alpha\,\beta\,\gamma...) \tag{2-1}$$

Only the minimum necessary number of indices will be retained. If several functions are considered, the common indices will be omitted.

The Hermitian scalar product of two functions $|i)$ and $|j)$ will be written as

$$\int \psi_i^* \psi_j \, d\tau = (i|j) = (j|i)^* \tag{2-2}$$

The matrix elements of an operator P will be written as

$$(i|P|j) = (\psi_i|P\,\psi_j) = (P^\dagger\,\psi_i|\psi_j) \tag{2-3}$$

For a Hermitian operator, $H = H^\dagger$,

$$(i|H|j) = (\psi_i|H\,\psi_j) = (H\,\psi_i|\psi_j) \tag{2-4}$$

while for a unitary operator $R^{-1} = R^\dagger$,

$$(i|R|j) = (\psi_i|R\,\psi_j) = (R^{-1}\,\psi_i|\psi_j) \tag{2-5}$$

Consider a set of basis functions $|\psi_1)$, $|\psi_2)$, ..., $|\psi_n)$. We shall assume that they form a complete orthonormal set, so that

$$(\psi_i|\psi_j) = \delta(i,j) \tag{2-6}$$

and an arbitrary function $|f)$ may be expanded in terms of those of the basic set

$$|f) = \sum_i |\psi_i)\,(\psi_i|f) \tag{2-7}$$

Similarly, the action of an operator R on the basis functions may be expressed in the form

$$R|\psi_j) = \sum_i |\psi_i)\,(\psi_i|R|\psi_j) \tag{2-8}$$

---

*Due to typographical limitations the usual angular brackets $<>$ will be replaced by parentheses ( ).

The coefficients $(\psi_i|\dot{R}|\psi_j)$ are the matrix elements of the operator R in that basis.

If we consider the basis functions as the elements of a row vector $\tilde{\Psi}$ and the transformed functions $R|\psi_i)$ as the elements of another row vector $R\,\tilde{\Psi}$, we can write the previous expression in matrix form.

$$R\,\tilde{\Psi} = \tilde{\Psi}\,\mathbf{D}(R) \tag{2-9}$$

It may be noticed that on the right-hand side the matrix $\mathbf{D}(R)$ appears as a post-multiplier.

If two operators, R and S, are applied in succession, we have

$$S\,[R\,\tilde{\Psi}] = S\,[\tilde{\Psi}\,\mathbf{D}(R)] = [S\,\tilde{\Psi}]\,\mathbf{D}(R)$$

$$\tag{2-10}$$

$$[S\,R]\,\tilde{\Psi} = \tilde{\Psi}\,[\mathbf{D}(S)\,\mathbf{D}(R)]$$

so that the matrix of the product (SR) is the product of the corresponding matrices, written in the same order.

If we make a change of basis

$$\tilde{\Psi}' = \tilde{\Psi}\,\mathbf{A} \tag{2-11}$$

the elements of $\mathbf{A}$ are the transformation coefficients

$$A_{ij} = (\psi_i|\psi_j') \tag{2-12}$$

The action of the operator R on the new basis functions is

$$R\,\tilde{\Psi}' = [R\,\tilde{\Psi}]\,\mathbf{A} = \tilde{\Psi}\,\mathbf{D}(R)\cdot\mathbf{A} = \tilde{\Psi}'\,\mathbf{A}^{-1}\,\mathbf{D}(R)\,\mathbf{A} \tag{2-13}$$

and therefore, the matrix of the operator R in the new basis is related to the old one by a similarity transformation

$$\mathbf{D}'(R) = \mathbf{A}^{-1}\,\mathbf{D}(R)\,\mathbf{A} \tag{2-14}$$

If the new basis functions also form an orthonormal set, the transformation is unitary,

$$\mathbf{A}^\dagger = \mathbf{A}^{-1} \tag{2-15}$$

and the matrix of R in the new basis is

$$\mathbf{D}'(R) - \mathbf{A}^\dagger\,\mathbf{D}(R)\,\mathbf{A} \tag{2-16}$$

2-2

While the matrix elements of an operator in two different basis are different, (2-16), we may ask whether there is an operator having the same matrix elements in the new basis as the old operator had in the old basis, that is

$$(\psi_i | P | \psi_j) = (A \psi_i | P' | A \psi_j) \tag{2-17}$$

If we multiply the operator P on the left by $A^\dagger (A^{-1})^\dagger$ and on the right by $A^{-1} A$ we shall have

$$(\psi_i | P | \psi_j) = (\psi_i | A^\dagger (A^{-1})^\dagger P A^{-1} A | \psi_j)$$

$$= (A \psi_i | (A^{-1})^\dagger P A^{-1} | A \psi_j) \tag{2-18}$$

Therefore, we obtain identical results with the operators

$$P \text{ in the basis } |\psi_i)$$

and

$$(A^{-1})^\dagger P A^{-1} \text{ in the basis } |A \psi_i)$$

and both descriptions are equivalent. For a unitary transformation

$$(A^{-1})^\dagger P A^{-1} = A P A^{-1} \tag{2-19}$$

# 3. GROUP-THEORETICAL CONSIDERATIONS

Let $|\psi_1\rangle$, $|\psi_2\rangle$, ...., $|\psi_d\rangle$ be an orthonormal set of functions which under the operations of a symmetry group transform into linear combinations of themselves

$$R\,|\psi_j\rangle = \Sigma_i\,|\psi_i\rangle\,(\psi_i|R|\psi_j) \tag{3-1}$$

or, in matrix notation,

$$R\,\widetilde{\Psi} = \widetilde{\Psi}\,D(R) \tag{3-2}$$

The group of matrices $D(R)$ constitute a representation of the group, and the set of functions $\widetilde{\Psi}$ is said to form a basis for the representation.

If we introduce a change of basis by means of a linear transformation (non-singular)

$$\widetilde{\Psi}' = \widetilde{\Psi}\,A \tag{3-3}$$

the new basis functions transform as

$$R\,\widetilde{\Psi}' = \widetilde{\Psi}'D'(R) \tag{3-4}$$

The matrices of both representations are related by the similarity transformation

$$D'(R) = A^{-1}\,D(R)\,A \tag{3-5}$$

and the two matrix representations are said to be equivalent.

For a given matrix representation, $D(R)$, the basis function $|\psi_i\rangle$ is said to belong to the i-th row of the representation, since its coefficients in the transformation expression (3-1) are the elements of the i-th row of the matrices $D(R)$. The other functions are called its partners. Notice that this definition is made in reference to a particular matrix presentation. If an equivalent matrix representation is chosen, such as that afforded by the matrices $D'(R)$, the function that belongs to the i-th row will be $|\psi_i'\rangle$.

One may also consider the operations of the group as acting on the physical operators involved in the problem, rather than on the basis functions. An equivalent description is obtained if the transform of an operator P under a (unitary) operation of the group is

$$P' = R\,P\,R^{-1} \tag{3-6}$$

3-1

As in the case of the basis functions, the operators may also be classified according to their transformation properties.

For a given matrix representation $D(R)$, if a set of operators $P_1, P_2, \ldots, P_d$ transform under the group operations in the form (compare with Eq. (3-1),

$$R P_j R^{-1} = \Sigma_i P_i (\psi_i | R | \psi_j) \tag{3-7}$$

they are said to belong to that representation, and in particular $P_i$ is said to belong to the i-th row.

Of special interest are the symmetric operators. According to the preceding definition, an operator $A$ is said to be symmetric if for every group operation

$$R A R^{-1} = A \tag{3-8}$$

or

$$R A = A R \tag{3-9}$$

that is, a symmetric operator commutes with all the operations of the group.

All the preceding considerations apply equally to both reducible and irreducible representations. For irreducible representations some important theorems apply, and we shall refer to them briefly.

In what follows, functions that belong to irreducible representations will be labelled by two indices, the first corresponding to the irreducible representation, the second to the particular row to which they belong. Other additional labels will be necessary in general, since there may be several sets of functions with the same transformation properties, but we shall omit them unless they are required. For an irreducible representation $\gamma$, the basis functions transform as

$$R |\gamma\mu) = \Sigma_\lambda |\gamma\lambda) (\gamma\lambda | R | \gamma\mu) \tag{3-10}$$

The orthogonality relations of irreducible representations may be written in the form

$$\Sigma_R (\gamma\mu | R^{-1} | \gamma\lambda) (\gamma'\lambda' | R | \gamma'\mu') = \frac{h}{d} \delta(\gamma,\gamma') \delta(\mu,\mu') \delta(\lambda,\lambda') \tag{3-11}$$

where $\underline{h}$ is the order of the group and $\underline{d}$ the dimension of the irreducible representation.

In what follows we shall assume that the matrix representations are unitary. In this case

$$D^{-1}(R) = D^\dagger(R)$$

$$(\gamma\mu | R^{-1} | \gamma\lambda) = (\gamma\lambda | R | \gamma\mu)^* \tag{3-12}$$

and the orthogonality relations take the form

$$\Sigma_R (\gamma\lambda|R|\gamma\mu)^* \; (\gamma'\lambda'|R|\gamma'\mu') = \frac{h}{d} \; \delta(\gamma,\gamma') \, \delta(\mu,\mu') \, \delta(\lambda,\lambda') \tag{3-13}$$

A very important theorem applying to the class of symmetric operators may be stated as follows:

The matrix elements of symmetric operators between functions that belong to different irreducible representations or to different rows of the same irreducible representation are zero.

The proof may be given briefly. Consider the sets of functions $|\alpha\gamma\mu)$ and $|\alpha'\gamma'\mu')$, the indices $\alpha$ and $\alpha'$ being necessary since we may have $\gamma = \gamma'$ and $\mu = \mu'$. Under the operations of the group they transform as

$$R|\alpha\gamma\mu) = \Sigma_{\lambda=1}^d \; |\alpha\gamma\lambda)\,(\gamma\lambda|R|\gamma\mu) \tag{3-14}$$

Also

$$AR|\alpha'\gamma'\mu') = \Sigma_{\lambda'=1}^{d'} \, A|\alpha'\gamma'\lambda')\,(\gamma'\lambda'|R|\gamma'\mu') \tag{3-15}$$

If we take the Hermitian product of (3-14) and (3-15) and consider that

$$R^\dagger A R = R^\dagger R A = A \tag{3-16}$$

we obtain

$$(\alpha\gamma\mu|A|\alpha'\gamma'\mu') =$$

$$\Sigma_\lambda \Sigma_{\lambda'} (\gamma\lambda|R|\gamma\mu)^* \, (\gamma'\lambda'|R|\gamma'\mu')\,(\alpha\gamma\lambda|A|\alpha'\gamma'\lambda') \tag{3-17}$$

By adding over all the operations of the group and introducing the orthogonality relations

$$h\,(\alpha\gamma\mu|A|\alpha'\gamma'\mu') = \Sigma_\lambda \Sigma_{\lambda'} (\alpha\gamma\lambda|A|\alpha'\gamma'\lambda')\frac{h}{d}\, \delta(\gamma,\gamma')\,\delta(\mu,\mu')\,\delta(\lambda,\lambda') \tag{3-18}$$

$$(\alpha\gamma\mu|A|\alpha'\gamma'\mu') = \delta(\gamma,\gamma')\,\delta(\mu,\mu')\,\Sigma_{\lambda=1}^d \frac{1}{d}\,(\alpha\gamma\lambda|A|\alpha'\gamma\lambda) \tag{3-19}$$

In addition, the right hand side is independent of $\mu$, so that it is the same for all partners.

In particular, since the unit operator is symmetric, functions that belong to different irreducible representations, or to different rows of the same irreducible representations, are orthogonal.

# 4. PROJECTION OPERATORS AND SYMMETRY FUNCTIONS

If we have an orthonormal set of basis functions for each of the irreducible representations of a group, the matrices of the operators R of the group, in the representation afforded by all those basis functions, of dimension $\underline{h}'$ $(= \sum_{\gamma} d_\gamma)$ are of the form

$$
\begin{bmatrix}
D^{(1)}(R) & 0 & 0 & 0 \\
0 & D^{(2)}(R) & 0 & 0 \\
 & & \ddots & \\
0 & 0 & D^{(\gamma)}(R) & 0 \\
 & & & \ddots \\
0 & 0 & 0 & D^{(\ )}(R)
\end{bmatrix}
\tag{4-1}
$$

We can express those matrices in terms of very simple ones if we consider that any matrix of order $\underline{d}$ may be expressed as a linear combination of $\underline{d}^2$ matrices of the same order, each of which contains only one non-vanishing element in a particular row and column. For example, any second order matrix may be expressed in terms of the four matrices

$$
\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad
\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}, \quad
\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \text{ and } \quad
\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}
\tag{4-2}
$$

These may be considered as the matrices of four operators $P_{11}$, $P_{22}$, $P_{12}$, and $P_{21}$ in the space of two basis functions $|1)$ and $|2)$. The transformation equation (2-9) takes now the forms

$$
[P_{11}|1), \; P_{11}|2)] = [|1), \; |2)] \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}
\tag{4-3}
$$

or
$$
P_{11}|1) = |1), \quad P_{11}|2) = 0
\tag{4-4}
$$

Similarly,
$$
[P_{12}|1), \; P_{12}|2)] - [|1), \; |2)] \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}
\tag{4-5}
$$

or
$$
P_{12}|1) = 0, \quad P_{12}|2) = |1)
\tag{4-6}
$$

In general,
$$
P_{\alpha\beta}|\beta') = |\alpha) \, \delta(\beta, \beta')
\tag{4-7}
$$

The operators $P_{\alpha\alpha}$ are "projection" operators, and the operators of the type $P_{\alpha\beta}$ are called "ladder" operators or "step" operators.

In our case, the matrices (4-1) of the operators R have at most $\underline{h}(= \Sigma_\gamma d_\gamma^2)$ non-vanishing matrix elements, and may be expressed in terms of $\underline{h}$ matrices of the type mentioned. The corresponding operators will be designated by $P_{\lambda\mu}^{(\gamma)}$ .

The fact that the only non-vanishing matrix element of $P_{\lambda\mu}^{(\gamma)}$ is the one in the $\lambda$-th row and the $\mu$-th column of the $\gamma$ representation may be expressed by

$$(\gamma\lambda |P_{\lambda\mu}^{(\gamma)}|\gamma'\mu') = \delta(\gamma,\gamma')\,\delta(\lambda,\lambda')\,\delta(\mu,\mu') \tag{4-8}$$

They operate on the basis functions

$$P_{\lambda\mu}^{(\gamma)}|\gamma'\mu') = |\gamma\lambda)\,\delta(\gamma,\gamma')\,\delta(\mu,\mu') \tag{4-9}$$

to give the same function, or a partner, or zero. They operate in the same form on each other

$$P_{\lambda\mu}^{(\gamma)}\,P_{\mu'\nu}^{(\gamma')} - P_{\lambda\nu}^{(\gamma)}\,\delta(\gamma,\gamma')\,\delta(\mu,\mu') \tag{4-10}$$

They are real

$$\left(P_{\lambda\mu}^{(\gamma)}\right)^* = P_{\lambda\mu}^{(\gamma)} \tag{4-11}$$

They are not Hermitian, but

$$\left(P_{\lambda\mu}^{(\gamma)}\right)^\dagger = P_{\mu\lambda}^{(\gamma)} \tag{4-12}$$

The relations between the $P_{\lambda\mu}^{(\gamma)}$ operators and the operators R of the group are easily established. From the previous considerations it is almost evident that

$$R = \Sigma_{\gamma,\lambda,\mu}\ P_{\lambda\mu}^{(\gamma)}\,(\gamma\lambda|R|\gamma\mu) \tag{4-13}$$

The inverse relation giving the operators $P_{\lambda\mu}^{(\gamma)}$ in terms of the R's is obtained by multiplying both sides of Eq. (4-13) by $(\gamma\lambda'|R|\gamma'\mu')^*$ and adding over all the group operations, taking into account the orthogonality relations

$$\Sigma_R (\gamma\lambda'|R|\gamma'\mu')^* R = \Sigma_{\gamma,\lambda,\mu} P_{\lambda\mu}^{(\gamma)} \Sigma_R\ (\gamma\lambda'|R|\gamma'\mu')^*\ (\gamma\lambda|R|\gamma\mu) = \frac{h}{d}\,P_{\lambda'\mu'}^{(\gamma')}$$

or

$$P_{\lambda\mu}^{(\gamma)} = \frac{d}{h}\,\Sigma_R\ (\gamma\lambda|R|\gamma\mu)^* R \tag{4-14}$$

It may be pointed out that the expression (4-14) of these operators depends on the particular matrix representation considered. This is only a reflection of the fact that the

projection operators are defined in reference to a particular choice of axis, or basis functions. One may also define a similar set of operators $P^{(\gamma)}$ bearing the same relation to the characters as the $P^{(\gamma)}_{\lambda\mu}$ bear to the elements of the irreducible representations.

$$P^{(\gamma)} = \Sigma_\lambda \; P^{(\gamma)}_{\lambda\lambda} = \frac{d}{h} \Sigma_R \; \chi^{(\gamma)} (R)^* \; R \qquad (4\text{-}15)$$

The expression (4-15) for these is independent of the particular form of the irreducible representations.

The sum of all the projection operators

$$E = \Sigma_{\gamma,\lambda} \; P^{(\gamma)}_{\lambda\lambda} \qquad (4\text{-}16)$$

has the unit matrix of order $h'$ as representative, and may therefore be considered as the unit operator.

Any arbitrary function on which the operators R may act, can be expanded as a sum of functions that belong to the different rows of the different irreducible representations.

$$|f) = \Sigma_{\gamma,\lambda} \; P^{(\gamma)}_{\lambda\lambda} |f) = \Sigma_{\gamma,\lambda} |f\gamma\lambda) \qquad (4\text{-}17)$$

The individual projection operators $P^{(\gamma)}_{\lambda\lambda}$ select from the function $|f)$ that part $|f\gamma\lambda)$ which transforms according to a particular row $\lambda$ of a certain irreducible representation $\gamma$,

$$P^{(\gamma)}_{\lambda\lambda} |f) = |f\gamma\lambda) \qquad (4\text{-}18)$$

The other operators $P^{(\gamma)}_{\lambda'\lambda}$, associated with the different rows of the same column, applied to $|f)$ generate the partners of $|f\gamma\lambda)$

$$P^{(\gamma)}_{\lambda'\lambda} |f) = |f\gamma\lambda') \qquad (4\text{-}19)$$

That $|f\gamma\lambda')$ is the $\lambda'$-th partner of $|f\gamma\lambda)$ follows easily from the fact that the operator $P^{(\gamma)}_{\lambda'\lambda}$ applied to the latter gives the former.

If the transformation of the function $|f)$ under the group operations R is known, the symmetry functions $|f\gamma\lambda)$ can be obtained explicitly by means of Eq. 4-14)

$$|f\gamma\lambda) = \frac{d}{h} \Sigma_R \; (\gamma\lambda|R|\gamma\lambda)^* \; R|f) \qquad (4\text{-}20)$$

$$|f\gamma\lambda') = \frac{d}{h} \Sigma_R \; (\gamma\lambda'|R|\gamma\lambda)^* \; R|f) \qquad (4\text{-}21)$$

These are the basic equations used to obtain symmetry functions by use of projection operators.

4-3

As a final remark we shall mention the fact that the operators associated with the different rows of any given column of an irreducible representation transform, on premultiplication by an operation of the group, into linear combinations of themselves and in exactly the same form as the basis functions.

By relabeling Eq. (4-13) and multiplying both sides by $P_{\mu\lambda}^{(\gamma)}$, we obtain

$$R\ P_{\mu\lambda}^{(\gamma)} = \Sigma_{\gamma',\lambda',\mu'}\ P_{\lambda'\mu'}^{(\gamma')}\ P_{\mu\lambda}^{(\gamma)}\ (\gamma'\lambda'|R|\gamma'\mu') \qquad (4\text{-}22)$$

and since

$$P_{\lambda'\mu'}^{(\gamma')}\ P_{\mu\lambda}^{(\gamma)} = P_{\lambda'\lambda}^{\gamma}\ \delta(\gamma,\gamma')\ \delta(\mu,\mu') \qquad (4\text{-}23)$$

it follows that

$$R\ P_{\mu\lambda}^{(\gamma)} = \Sigma_{\lambda'}\ P_{\lambda'\lambda}^{(\gamma)}\ (\gamma\lambda'|R|\gamma\mu) \qquad (4\text{-}24)$$

This may be compared with the transformation of the basis functions, Eq.(3-10)

$$R|\gamma\mu) = \Sigma_{\lambda'}\ |\gamma\lambda')\ (\gamma\lambda'|R|\gamma\mu) \qquad (4\text{-}25)$$

Symmetric operators commute with all the $P_{\lambda\mu}^{(\gamma)}$. This follows from the definition of symmetric operators (Eqs. 3-8, 9) and the fact that the $P_{\lambda\mu}^{(\gamma)}$ are linear combinations of the operations of the group (Eq. 4-14). If A is symmetric,

$$A\ P_{\lambda\mu}^{(\gamma)} = P_{\lambda\mu}^{(\gamma)}\ A \qquad (4\text{-}26)$$

## SYMMETRY FUNCTIONS

A more general problem than the expansion of a function in terms of symmetry functions, in the form of Eq. (4-17), is the following: Given a set of functions $|f_1)$, $|f_2)$, . . . , $|f_n)$ whose transformations under the operations of a group are known, it is desired to find the linear combinations of them which belong to the different rows of the irreducible representations of the group. This problem presents itself whenever the Hamiltonian or other physical operators of interest are invariant or have some definite symmetry properties. It is desirable to make a linear transformation from the original basis to a basis composed of symmetry functions.

We shall always assume that the given set of functions form an orthonormal basis for a representation of the group. This implies that the transformed functions $R|f_i)$ can always be expressed as a linear combination of functions which are all part of the initial

set. Otherwise, the basis should be completed by including the necessary number of independent functions generated by the action of the group operations on the $|f_i)$ which are orthogonal to them (and among themselves).

If the characters of the representation (generally reducible) afforded by the functions $|f_i)$ are designated by $\chi(R)$, the number of independent sets of partner functions belonging to the representation $\gamma$, is given by the familiar expression

$$n_\gamma = \frac{1}{h} \sum_R \chi^{(\gamma)}(R)^* \cdot \chi(R) \tag{4-27}$$

Accordingly, if an operator $P^{(\gamma)}_{\lambda\mu}$ is applied to all the functions of the set $|f_i)$, the number of non-vanishing symmetry functions $|f_i \gamma \lambda)$ generated is greater than or equal to $n_\gamma$. The required number $n_\gamma$ of symmetry functions may be chosen quite arbitrarily, provided they are independent, and the selected functions may be orthogonalized by any of the usual methods. Actually, in virtue of some convenient properties of these operators, it is advantageous to carry out the selection and the orthogonalization concurrently, thus insuring also the linear independence of the selected symmetry functions. In order to illustrate the method, let us first consider the conditions for the orthogonality between functions generated by a given operator, $P^{(\gamma)}_{\lambda\mu}$.

The Hermitian product of the functions $P^{(\gamma)}_{\lambda\mu}|f)$ and $P^{(\gamma)}_{\lambda\mu}|g)$ is, according to Eqs. (4-12) and (4-10)

$$(f|P^{(\gamma)}_{\mu\lambda} \; P^{(\gamma)}_{\lambda\mu}|g) = (f|P^{(\gamma)}_{\mu\mu}|g) \tag{4-28}$$

and therefore, orthogonality between $|f)$ and $|g)$ does not entail the orthogonality of the "projected" functions. These are orthogonal only if $|f)$ is orthogonal to $P^{(\gamma)}_{\mu\mu}|g)$, and consequently $|g)$ to $P^{(\gamma)}_{\mu\mu}|f)$. In reference to any two functions of the initial set, since

$$P^{(\gamma)}_{\mu\mu}|f_i) = \sum_j |f_j) \, (f_j|P^{(\gamma)}_{\mu\mu}|f_i) \tag{4-29}$$

the orthogonality between $P^{(\gamma)}_{\lambda\mu}|f_i)$ and $P^{(\gamma)}_{\lambda\mu}|f_j)$ implies that $P^{(\gamma)}_{\mu\mu}|f_i)$ does not "contain" $|f_j)$, and conversely, that $P^{(\gamma)}_{\mu\mu}|f_j)$ does not contain $|f_i)$. It may be noticed that the result is independent of $\lambda$, so that all the pairs of corresponding partner functions generated from $|f_i)$ and $|f_j)$ have the same Hermitian scalar product. (Cf. Eq. 3-19)

The orthogonalization process may then be carried out as follows:

a)  Select a function $|g_1)$, which may be one of the initial functions or a linear combination of them.

b)  Let all the $P_{\lambda\mu}^{(\gamma)}$ associated with a certain column $\mu$ operate on $|g_1)$. The symmetry set of functions obtained may be taken as one of the $n_\gamma$ possible sets.

c)  Select a function $|g_2)$, orthogonal to any $P_{\lambda\mu}^{(\gamma)}|g_1)$, say to $P_{\nu\mu}^{(\gamma)}|g_1)$.

d)  Let all the $P_{\lambda\nu}^{(\gamma)}$ associated with the column $\nu$ operate on $|g_2)$. The set of symmetry functions obtained will be orthogonal to the previous one.  ·

e)  Select a function $|g_3)$, orthogonal to $P_{\rho\mu}^{(\gamma)}|g_1)$ and $P_{\rho\nu}^{(\gamma)}|g_2)$, etc.

The preceding sequence of operations should be continued until the $n_\gamma$ independent symmetry sets have been obtained. The process may be carried out by using only the operators associated with one column ($\mu = \nu = \rho = \ldots.$), but the freedom of choice is often important to simplify the process.

It may happen that one of the functions selected is such that $P_{\lambda\mu}^{(\gamma)}|g_i) = 0$. If it is zero for one value of $\lambda$, it will vanish also for all others, since

$$P_{\nu\lambda}^{(\gamma)} \ P_{\lambda\mu}^{(\gamma)}|g_i) \ = \ P_{\nu\mu}^{(\gamma)}|g_i) \ = \ 0 \tag{4-30}$$

This implies that the function $|g_i)$ does not contain any of the possible functions belonging to the row $\mu$, or that it is orthogonal to them. One may then select a new $|g_i)$ function orthogonal to the old one as well as to all previous symmetry functions $P_{\mu\sigma}^{(\gamma)}|g_j)$ which belong to the row $\mu$, and continue the orthogonalization process.

The symmetry functions $P_{\lambda\mu}^{(\gamma)}|g_i)$ are not normalized, but the normalizing factor N is easily determined. The Hermitian scalar product of one of the symmetry functions with itself is

$$N^2 \ = (g_i|P_{\mu\lambda}^{(\gamma)} \ P_{\lambda\mu}^{(\gamma)}|g_i) = (g_i|P_{\mu\mu}^{(\gamma)}|g_i) \tag{4-31}$$

This is the same for all partners, as the result is independent of $\lambda$.

If the function is one of the initial $|f_i)$ this result is especially simple, as $(f_i|P_{\mu\mu}^{(\gamma)}|f_i)$ is the coefficient of $|f_i)$ itself in the expression (4-29) for $P_{\mu\mu}^{(\gamma)}|f_i)$. The normalized symmetry functions are given by

$$(f_i|P_{\mu\mu}^{(\gamma)}|f_i)^{-\frac{1}{2}} \ P_{\lambda\mu}^{(\gamma)}|f_i) \tag{4-32}$$

Once the symmetry functions have been determined, the change of basis may be performed by means of the transformation

$$P_{\lambda\mu}^{(\gamma)}|g_j) = \sum_i |f_i) (f_i|P_{\lambda\mu}^{(\gamma)}|g_j) \tag{4-33}$$

As already mentioned, the only non-vanishing elements of symmetric operators in the new basis are those between functions which belong to the same row of the same irreducible representation, Eq. (3-20)

There is a further important theorem arising from the fact that symmetric operators commute with all the $P_{\lambda\mu}^{(\gamma)}$, (Eq. 4-26), and from the multiplication properties of these operators (Eq. 4-10). If the symmetry functions are obtained by means of the projection operators, the matrix elements may be simplified as follows

$$(P_{\lambda\mu}^{(\gamma)}g_i| \ A \ | \ P_{\lambda\nu}^{(\gamma)}g_j) = (g_i|P_{\mu\lambda}^{(\gamma)} \ A \ | \ P_{\lambda\nu}^{(\gamma)}g_j) = (g_i| \ A \ |P_{\mu\lambda}^{(\gamma)}P_{\lambda\nu}^{(\gamma)}g_j)$$

$$= (g_i| \ A \ | \ P_{\mu\nu}^{(\gamma)}g_j) = (P_{\nu\mu}^{(\gamma)}g_i| \ A \ | \ g_j) \tag{4-34}$$

In particular, if only the operators $P_{\lambda\mu}^{(\gamma)}$ corresponding to the column $\mu$ are used

$$(P_{\lambda\mu}^{(\gamma)}g_i| \ A \ | \ P_{\lambda\mu}^{(\gamma)}g_j) = (g_i| \ A \ | \ P_{\mu\mu}^{(\gamma)} \ g_j) = (P_{\mu\mu}^{(\gamma)}g_i \ | \ A \ | \ g_j) \tag{4-35}$$

As might be expected, the results are also independent of the particular row, $\lambda$, of the representation.
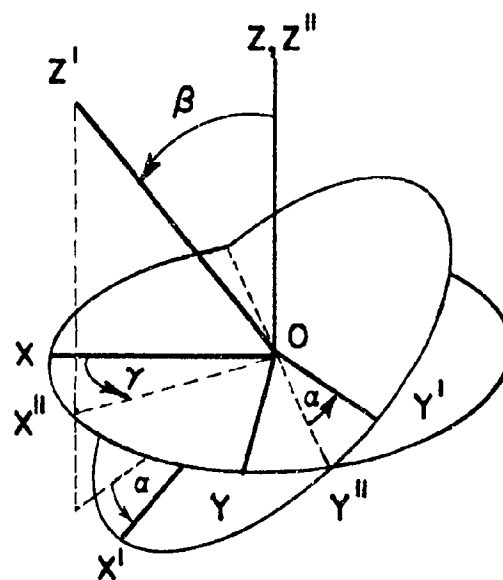
EULER'S ANGLES

FIG. 5-1

# 5. TRANSFORMATION OF THE ANGULAR MOMENTUM EIGENFUNCTIONS UNDER ROTATIONS

A rotation of the frame of reference that brings the set of axes $x, y, z$, into coincidence with the new set $x', y', z'$, may be considered as the product of three successive rotations by the Eulerian angles $\alpha, \beta, \gamma$, that may be described as follows:

a) A rotation by $\gamma$ about the $z$-axis, leading to the intermediate set of axes $x'', y'', z''$.

b) A rotation by $\beta$ about the intermediate $y''$-axis.

c) A rotation by $\alpha$ about the new $z'$-axis, leading the final set of axes $x', y', z'$.

These operations are illustrated in Fig. 5-1. All rotations are considered in the positive sense. We may write the transformation matrix, Eq. (1-18) as the product

$$R(\alpha\beta\gamma) = \mathbf{R}_{z'}(\alpha) \, \mathbf{R}_{y''}(\beta) \, \mathbf{R}_{z}(\gamma) \tag{5-1}$$

The corresponding product of operators, defined as in Eq. (1-17) is

$$R(\alpha\beta\gamma) = R_{z}(\alpha) \, R_{y}(\beta) \, R_{z}(\gamma) \tag{5-2}$$

The usual ranges for the Eulerian angles are

$$0 \leq \alpha < 2\pi$$

$$0 \leq \gamma < 2\pi \tag{5-3a}$$

$$0 \leq \beta \leq \pi$$

but for $\beta = 0$, the only other parameter necessary to specify the rotation is $\alpha + \gamma$ and similarly, for $\beta = \pi$ only the difference $\alpha - \gamma$ is relevant.

This choice of limits insures a one to one correspondence between the sets of values of the parameters and the rotations of a rigid body. Other choices of limits are possible.

When considering the transformation under rotations of the angular momentum eigenfunctions, a rotation by $2\pi$ about any axis is no longer the unit operation, as the

eigenfunctions for half-integral quantum numbers are transformed into their negatives. The transformations of the angular momentum eigenfunctions to be considered are those of the two-dimensional unitary group, rather than the three-dimensional pure rotation group.[4]

The familiar language about rotations may be preserved if, proceeding as Bethe,[5] the range for the angle of rotation about a given axis is extended to $0 \leq \phi < 4\pi$, and rotations by angles differing by $2\pi$ are no longer considered equivalent.

The correspondence between these generalized rotations and the sets of Eulerian angles can also be insured by an appropriate choice of limits. A convenient, symmetric choice is, for example

$$-\pi < \alpha + \gamma \leq \pi$$

$$-\pi < \alpha - \gamma \leq \pi \tag{5-3b}$$

$$-2\pi < \beta \leq 2\pi$$

To every set of parameters in these intervals there corresponds a unitary transformation or generalized rotation.

The theory of the angular momentum and that of rotations in three-dimensional space are very closely connected. The eigenfunctions $|jm\rangle$ may be derived as eigenfunctions of the operators $J^2$ and $J_z$, and also as basis functions for the irreducible representations for the three-dimensional rotation group. The relation between the operator $R_n(\theta)$, associated with a rotation by an angle $\theta$ about an axis defined by the unit vector $n$, and the operators $n \cdot J$ of the component of the angular momentum along the axis of rotation is given by[1-3]

$$R_n(\theta) = e^{i\theta(n \cdot J)} \tag{5-4}$$

so that, for example

$$R_z(\alpha) = e^{i\alpha J_z}, \quad R_y(\beta) = e^{i\beta J_y} \tag{5-5}$$

The rotation operators commute with $J^2$. Also, the operator associated with a rotation about a certain axis commutes with the operator of the component of $J$ along that axis.

Accordingly, the angular momentum eigenfunctions $|jm\rangle$ transform into eigenfunctions of $J^2$ with the same eigenvalue, $j$, under all rotations. For rotations about the z-axis, the eigenvalue $m$ of $J_z$ is also preserved, the eigenfunction being only multiplied by a phase factor

$$R_z(a) \, |jm) = |jm) \, e^{im a} \tag{5-6}$$

However, a rotation about any other axis will change the direction of the axis of quantization and consequently the eigenvalue, m, of the $J_z$ component. In general, the transformed function will be a linear combination of functions $|jm')$, with $\underline{m}'$ ranging from $-j$ to $j$. For example, the transformation equation for a rotation about the $\underline{y}$-axis is

$$R(0\beta 0) \, |jm) = \sum_{m'} |jm') \, (jm'|R(0\beta 0)|jm)$$

$$= \sum_{m'} |jm') \, d_{m'm}^{(j)}(\beta) \tag{5-7}$$

In the general case,

$$R(\alpha\beta\gamma) \, |jm) = \sum_{m'} |jm') \, (jm'|R(\alpha\beta\gamma)|jm)$$

$$= \sum_{m'} |jm') \, D_{m'm}^{(j)}(\alpha\beta\gamma) \tag{5-8}$$

If the rotation is expressed as the product $R_z(\alpha) \, R_y(\beta) \, R_z(\gamma)$ and Eqs. (5-6) and (5-7) are introduced, we can write

$$R(\alpha\beta\gamma) \, |jm) = \sum_{m'} |jm') \, e^{im'\alpha} \, d_{m'm}^{(j)}(\beta) \, e^{im\gamma} \tag{5-9}$$

This transformation matrices are irreducible representations of the three-dimensional rotation group or, more precisely, of the two-dimensional unitary group.[4] Explicit expressions for the matrix elements in terms of the three Eulerian angles have been given in the literature.[1-3] The definitions used by different authors are slightly different. The conventions we have followed are those of Wigner[1] and Edmonds.[2]

$$d_{m'm}^{(j)}(\beta) = \left[ \frac{(j+m)!(j-m)!}{(j+m')!(j-m')!} \right]^{1/2} \left( \cos \frac{\beta}{2} \right)^{2j} \sum_{\nu} (-1)^{\nu} \binom{j-m'}{\nu} \binom{j+m'}{m'-m+\nu} \left( \tan \frac{\beta}{2} \right)^{m'-m+2\nu} \tag{5-10}$$

the summation index, $\nu$, assumes all integral values for which the arguments of the factorials are non-negative.

The rotation matrices have certain symmetries arising from their unitary character and the choice of basis functions. They are obtained very easily from the symmetry properties of the matrices for the components of the angular momentum.

With the usual choice of phases, the only non-vanishing elements of $J_z$, $J_x$, and $J_y$, are of the form

$$(jm|J_z|jm) = m$$

$$(j, m \pm 1|J_x|jm) = \frac{1}{2} [(j \mp m)(j \pm m + 1)]^{1/2} \qquad (5\text{-}11)$$

$$(j, m \pm 1|J_y|jm) = \mp \frac{i}{2} [(j \mp m)(j \pm m + 1)]^{1/2}$$

The first symmetry property

$$(jm'|J_\mu|jm) = (jm|J_\mu|jm')^* \qquad (\mu = x, y, z) \qquad (5\text{-}12)$$

simply expresses the Hermitian character of these operators, and is shared by all their integral powers, $(J_\mu)^k$.

The second symmetry property gives the relation between complex conjugation and a change in sign of the projection quantum numbers (inversion of rows and columns).

$$(jm'|J_\mu|jm)^* = (-1)^{m'-m+1} (j, -m'|J_\mu|j, -m) \qquad (5\text{-}13)$$

For the integral powers, this relation takes the form

$$(jm'|(J_\mu)^k|jm)^* = (-1)^{m'-m+k} (j, -m'|(J_\mu)^k|j, -m) \qquad (5\text{-}14)$$

and we also have

$$(jm'|(iJ_\mu)^k|jm)^* = (-1)^{m'-m} (j, -m'|(iJ_\mu)^k|j, -m) \qquad (5\text{-}15)$$

For the rotation operators

$$R_\mu(\theta) = e^{i\theta J_\mu} = \sum_{k=0}^{\infty} \frac{1}{k!} (iJ_\mu)^k \qquad (5\text{-}16)$$

the first symmetry relation corresponds now to the unitary character of $R_\mu(\theta)$, and the second takes the same form of Eq. (5-15). In summary, the two independent symmetry relations of the matrix elements of the rotation operators are

$$(jm'|R|jm) = (jm|R^{-1}|jm')^*$$

$$(jm'|R|jm) = (-1)^{m'-m} (j,-m'|R|j,-m)^*$$  (5-17)

In particular, for rotations about the y-axis, the matrix elements are real, and

$$d^{(j)}_{m'm}(-\beta) = d^{(j)}_{mm'}(\beta)$$  (5-18)

For every value of $\beta$, the symmetry relations connect four elements, as follows

$$d^{(j)}_{m'm}(\beta) = d^{(j)}_{-m,-m'}(\beta) = (-1)^{m'-m} d^{(j)}_{mm'}(\beta) = (-1)^{m'-m} d^{(j)}_{-m',-m}(\beta)$$  (5-19)

The explicit expressions for some particular values of $\beta$ are of interest

$$d^{(j)}_{m'm}(0) = \delta(m',m)$$

$$d^{(j)}_{m'm}(\pi) = (-1)^{j+m} \delta(m',-m)$$  (5-20)

We shall also make use of the relations

$$d^{(j)}_{m'm}(\beta + \pi) = (-1)^{j-m'} d^{(j)}_{-m'm}(\beta)$$

$$d^{(j)}_{m'm}(\pi - \beta) = (-1)^{j-m'} d^{(j)}_{m',-m}(\beta)$$  (5-21)

The matrices for $\beta = \frac{\pi}{2}$ are of special interest. They appear as coefficients in the linear combinations that belong to the different irreducible representations of the cubic point groups. They are also convenient in problems involving coordinate transformations. The matrices for rotations $R(0\beta0)$ are, in general, tedious to compute. Their elements may be expressed in terms of rotations which involve only rotations about the y-axis by $\pi/2$, together with rotations about the z-axis, the latter being diagonal in the usual representation. The relation is[2]

$$R(0\beta0) = R(-\frac{\pi}{2}00) R(0,-\frac{\pi}{2},0) R(\beta00) R(0 \frac{\pi}{2} 0) R(\frac{\pi}{2} 00)$$  (5-22)

For $\beta = \frac{\pi}{2}$, there is a further symmetry relation, in addition to Eqs. (5-19). This follows from the last of Eqs. (5-21)

5-5

$$d_{m'm}^{(j)}\left(\frac{\pi}{2}\right) = (-1)^{j-m'} d_{m',-m}^{(j)}\left(\frac{\pi}{2}\right) \qquad (5\text{-}23)$$

This implies that, for a given value of j, only the elements in a certain region of the matrix, such as the shaded region in Fig. 5-2, need be calculated from Eq. (5-10).
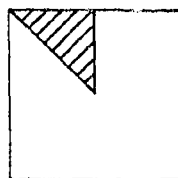


FIG. 5-2

Tables of $d_{m'm}^{(j)}\left(\frac{\pi}{2}\right)$ up to j = 2 are given by Edmonds.[2] Since these matrix elements are necessary for the purposes previously indicated, we have computed a table including values up to j = 12.5. The results are given in exact form, expressed as square roots of integers, which are also given as products of prime factors.

In problems involving correlations between cubic and trigonal symmetry, values of $d_{m'm}^{(j)}(\tau)$, where $\tau$ is the tetrahedral angle, are necessary. These have also been computed up to j = 12.5. Also, we have computed values of $d_{m'm}^{(j)}\left(\frac{\pi}{2}\right)$ up to j = 7.

Further details on the computations are given immediate preceding the tables.

*Relation with the spherical harmonics*

The elements of the rotation matrices $D_{mk}^{(j)}(\alpha\beta\gamma)$ are functions of a more general nature than the spherical harmonics. They are in fact the eigenfunctions of the symmetric rotor (Ref. 1, p. 214) The indices m and k are the eigenvalues of the projection of the angular momentum on the space-fixed z-axis and on the body-fixed symmetry axis, respectively.

Since they are the elements of a unitary matrix they satisfy the orthonormality relations

$$\sum_m D_{mk}^{(j)}(\alpha\beta\gamma)^* \ D_{mk'}^{(j)}(\alpha\beta\gamma) = \delta(k,k')$$

$$\sum_k D_{mk}^{(j)}(\alpha\beta\gamma)^* \ D_{m'k}^{(j)}(\alpha\beta\gamma) = \delta(m,m') \qquad (5\text{-}24)$$

Also, the $D_{mk}^{(j)}$ are orthogonal functions on the surface of the unit sphere. This follows from the fact that they are the elements of the irreducible representation matrices of the two-dimensional unitary group. The orthogonality relations take the form

5-6

$$\int D_{mk}^{(j)} (R)^* \, D_{m'k'}^{(j')} (R) \, dR = \frac{h}{2j+1} \, \delta(j,j') \, \delta(m,m') \, \delta(k,k') \tag{5-25}$$

where

$$h = \int dR = 8\pi^2$$

The relation between the spherical harmonics and the matrix elements of the rotation matrices is easily established. In the present case, Eq. (1-4) takes the form

$$Y_\ell^m (\theta,\phi) = R(\alpha\beta\gamma) \, Y_\ell^m (\theta',\phi') \tag{5-26}$$

The matrix elements of the rotation matrices are defined by Eq. (5-9), which is now

$$R(\alpha\beta\gamma) \, Y_\ell^m (\theta',\phi') = \sum_{m'} Y_\ell^{m'} (\theta',\phi') \, D_{m'm}^{(\ell)} (\alpha\beta\gamma) \tag{5-27}$$

so that

$$Y_\ell^m (\theta,\phi) = \sum_{m'} Y_\ell^{m'} (\theta',\phi') \, D_{m'm}^{(\ell)} (\alpha\beta\gamma) \tag{5-28}$$

In particular, we may consider the rotation of the coordinate axes such that the point on the unit sphere with original coordinates $\theta, \phi$ has in the new reference system the new coordinates $\phi' = 0, \theta' - 0$. Since the point in question lies on the new z-axis, the first and second Eulerian angles of the rotation are $\gamma = \phi$ and $\beta = \theta$. The third angle is arbitrary. Since the only spherical harmonic different from zero at $\phi' = 0, \theta' = 0$ is

$$Y_\ell^0 (0,0) = \left( \frac{2\ell+1}{4\pi} \right)^{1/2} \tag{5-29}$$

only one term on the right-hand side of Eq. (5-28) survives, and we have

$$Y_\ell^m (\theta,\phi) = \left( \frac{2\ell+1}{4\pi} \right)^{1/2} D_{0m}^{(\ell)} (\alpha\theta\phi) \tag{5-30}$$

$$= \left( \frac{2\ell+1}{4\pi} \right)^{1/2} d_{0m}^{(\ell)} (\theta) \, e^{im\phi}$$

By use of the symmetry relations we also obtain

$$Y_\ell^m (\theta,\phi) = \left( \frac{2\ell+1}{4\pi} \right)^{1/2} (-1)^m \, D_{m0}^{(\ell)} (\phi\theta\gamma) \tag{5-31}$$

where $\gamma$ is an arbitrary angle.

# 6. POINT GROUPS

## A. SINGLE GROUPS

The symmetry operations of the point groups may be classified into four different types:

a) Proper rotations about an axis of symmetry.

b) Inversion through a center of symmetry.

c) Reflections in a symmetry plane.

d) Improper rotations about an alternating axis of symmetry.

The last two types of operations may be considered as the product of the inversion and a proper rotation.

A reflection is equivalent to a rotation by 180° about an arbitrary axis perpendicular to the plane of symmetry, followed by the inversion through the intersection point.

An improper rotation by an angle $\phi$ is equivalent to a proper rotation by $\phi + \pi$ followed by an inversion through the orgin.

The inversion commutes with all symmetry operations.

The structure of the point groups fits into a simpler scheme if all the different operations are classified into the two following types:

a) Proper rotations.

b) Products of the inversion and a proper rotation.

The point groups $C_n$, $D_n$, T, and O, consist only of proper rotations. The rest are either isomorphous with one of these or the direct product of a rotation group and the inversion group.

A comprehensive symmary of the point groups and their operations, with the exception of the icosahedral, is given in Table 6-1. They are classified into three main groups, according to the possible values of the Eulerian angle $\beta$ of the rotations. The principal symmetry axis is chosen as z-axis.

Under the headings for each point group are listed the operations. Rotations with $\beta = 0$ are designated simply as $R_z(\phi)$ where $\phi$ corresponds to the value of $\alpha + \gamma$.

6-1

# TABLE 6-1

## SYMMETY OF THE POINT GROUPS

### CYCLIC AND RELATED GROUPS: $(\beta = 0)$

$$\phi_k = \frac{2\pi}{n} k$$

| n OPERATIONS | 2n OPERATIONS | | | |
|---|---|---|---|---|
| Cyclic Groups | Direct Product $I \times C_n$ | | Isomorphous with $C_{2n}$ | |
| | n odd | n even | n even | n odd |
| $C_n$ | $S_{2n}$ | $C_{nh}$ | $S_{2n}$ | $C_{nh}$ |
| $R_z(\phi_k)$ | $R_z(\phi_k)$ | | $R_z(\phi_k)$ | |
| | $I \cdot R_z(\phi_k)$ | | $I \cdot R_z(\phi_k \pm \frac{\pi}{n})$ | |

### DIHEDRAL AND RELATED GROUPS: $(\beta = 0, \pi)$

$$\phi_k = \frac{2\pi}{n} k$$

| 2n OPERATIONS | | 4n OPERATIONS | | | |
|---|---|---|---|---|---|
| Dihedral Groups | Isomorphous with $D_n$ | Direct Product $I \times D_n$ | | Isomorphous with $D_{2n}$ | |
| | | n odd | n even | n even | n odd |
| $D_n$ | $C_{nv}$ | $D_{nd}$ | $D_{nh}$ | $D_{nd}$ | $D_{nh}$ |
| $R_z(\phi_k)$ | $R_z(\phi_k)$ | $R_z(\phi_k)$ | | $R_z(\phi_k)$ | |
| $R(\phi_k, \pi)$ | | $R(\phi_k, \pi)$ | | $R(\phi_k, \pi)$ | |
| | | $I \cdot R_z(\phi_k)$ | | $I \cdot R_z(\phi_k \pm \frac{\pi}{n})$ | |
| | $I \cdot R(\phi_k, \pi)$ | $I \cdot R(\phi_k, \pi)$ | | $I \cdot R(\phi_k \pm \frac{\pi}{n}, \pi)$ | |

### CUBIC GROUPS: $(\beta = 0, \pi, \frac{\pi}{2})$

$$\alpha, \gamma = 0, \pi, \pm \frac{\pi}{2}$$

| | 12 OPERATIONS | 24 OPERATIONS | | | 48 OPERATIONS |
|---|---|---|---|---|---|
| | Rotation Group $T$ | Rotation Group $O$ | Isomorphous with 0 $T_d$ | Direct Product $I \times T$ $T_h$ | Direct Product $I \times 0$ $O_h$ |
| $(\pm\alpha \pm \beta \pm \gamma) = k\pi$ | $R(\alpha\beta\gamma)$ | $R(\alpha\beta\gamma)$ | $R(\alpha\beta\gamma)$ | $R(\alpha\beta\gamma)$ $I \cdot R(\alpha\beta\gamma)$ | $R(\alpha\beta\gamma)$ $I \cdot R(\alpha\beta\gamma)$ |
| $(\pm\alpha \pm \beta \pm \gamma) = k\pi + \frac{\pi}{2}$ | | $R(\alpha\beta\gamma)$ | $I \cdot R(\alpha\beta\gamma)$ | | $R(\alpha\beta\gamma)$ $I \cdot R(\alpha\beta\gamma)$ |

Rotations with $\beta = \pi$ are designated as $R(\phi, \pi)$, where $\phi$ corresponds now to $\alpha - \gamma$. The angles $\phi_k$ are of the form

$$\phi_k = \frac{2\pi}{n} k \qquad (6\text{-}1)$$

and k assumes the n possible integral values in the interval

$$-\frac{1}{2} n < k \leq \frac{1}{2} n \qquad (6\text{-}2)$$

For those operations with rotation angles $\phi = \phi_k \pm \frac{\pi}{n}$, only one sign need be chosen. If the convention $-\pi < \phi \leq \pi$ is followed, the minus sign may be chosen for n even, the plus sign for n odd.

For the cubic groups, the possible values for the angles of the rotations $R(\alpha\beta\gamma)$ are specified by the conditions given in the first column.

## B. DOUBLE GROUPS

We have already seen that the existence of angular momentum eigenfunctions with half-integral quantum numbers lead to the consideration of their transformation properties under the operations of the two-dimensional unitary group, rather than the three-dimensional pure rotation group.

Similarly, the transformation matrices of those eigenfunctions under the operations of a point group do not afford a representation of the group. However, these matrices, together with their negatives, form a (matrix) group with twice as many operations as the point group. The group of operations isomorphous with that matrix group is called[5] the "double group" of the point group in question.

To every operation R of the "single" group there correspond two operations of the double group that may be designated as R and $\overline{R}$. The number of classes and irreducible representations is not always double.[5,6] We shall give the irreducible representations in the sections dealing with the individual groups.

All the representations afforded by $|jm\rangle$ eigenfunctions with integral quantum numbers (the integral representations) have identical matrices for R and $\overline{R}$, being also representations of the single group. For all the representations afforded by $|jm\rangle$ functions with half-integral quantum numbers (the half-integral representations) the matrices of R and $\overline{R}$ are the negative of each other.

6-3

The definition of the operations R and $\bar{R}$, although arbitrary to a certain extent, may be made in a consistent form by appropriate conventions as to the choice of parameters. For example, with the choice of limits for the Eulerian angles given by Eqs. (5-3b)

$$-\pi < \alpha + \gamma \leq \pi$$

$$-\pi < \alpha - \gamma \leq \pi \qquad (6\text{-}3)$$

$$-2\pi < \quad \beta \quad \leq 2\pi$$

we may define the operations R by requiring the angle $\beta$ to be within the limits

$$-\pi < \beta \leq \pi \qquad (6\text{-}4)$$

while the operations $\bar{R}$ will then correspond to values of $\beta$ outside this interval.

Since the rotation matrices satisfy the equation

$$D^{(j)}(\alpha\beta\gamma) = (-1)^{2j} D^{(j)}(\alpha, \beta \pm 2\pi, \gamma) \qquad (6\text{-}5)$$

this establishes a one to one correspondence between the points in both regions, as well as the proper relations between representation matrices.

For a rotation by an angle $\phi$ about any arbitrary axis, the trace of the matrices for $j = \frac{1}{2}$ is

$$\chi^{(1/2)} = \frac{\sin \phi}{\sin \frac{1}{2} \phi} = 2 \cos \frac{\beta}{2} \cos \frac{\alpha + \gamma}{2} \qquad (6\text{-}6)$$

Therefore, according to the previous definition the operations R correspond to angles of rotation $-\pi < \phi \leq \pi$ and have non-negative characters for the $E_{1/2}$ representation.

The operations of the double point groups may be obtained from those of the single point groups given in Table 6-1 by an extension of the limits for the angles. The number of operations of each type is doubled, but the relations of isomorphism or direct product are equally valid for the double groups.

For the cyclic, dihedral, and related groups the new operations are most simply defined by extending the allowed interval for the angles $\phi_k$ to

$$-2\pi < \phi_k \leq 2\pi \qquad (6\text{-}7)$$

6-4

with k assuming now the 2n integral values in the interval

$$-n < k \leq n \tag{6-8}$$

Although the operations R and $\bar{R}$ may be defined in a consistent way, by assigning to them different sets of Eulerian angles, according to appropriate conventions, it may be pointed out that this is not strictly necessary for most practical purposes.

Consider, for example, the fundamental problem of expanding an arbitrary function $|f)$ as a sum of terms each of which belongs to a particular row of an irreducible representation of the symmetry group

$$|f) = \sum_{\gamma,\lambda} |f\gamma\lambda) \tag{6-9}$$

The different terms in the expansion are obtained, as indicated in Eqs. (4-17) and (4-18), by applying the corresponding projection operator

$$|f\gamma\lambda) = P_{\lambda\lambda}^{(\gamma)} |f) = P_{\lambda\lambda}^{(\gamma)} |f\gamma\lambda) \tag{6-10}$$

For the double groups we may use the expression for the projection operators (4-20) in the form

$$P_{\lambda\lambda}^{(\gamma)} |f) = \frac{d}{h} \sum_R [(\gamma\lambda|R|\gamma\lambda)^* R + (\gamma\lambda|\bar{R}|\gamma\lambda)^* \bar{R}] |f\gamma\lambda) \tag{6-11}$$

where h is the number of operations of the double group. But from the definition of the R and $\bar{R}$ operations we have

$$(\gamma\lambda|R|\gamma\lambda) = \pm (\gamma\lambda|\bar{R}|\gamma\lambda)$$

$$R|f\gamma\lambda) = \pm \bar{R}|f\gamma\lambda) \tag{6-12}$$

with the plus signs if $\gamma$ is an integral representation, and the minus signs if it is a half-integral representation. In every case, however,

$$(\gamma\lambda|R|\gamma\lambda)^* R|f\gamma\lambda) = (\gamma\lambda|\bar{R}|\gamma\lambda)^* \bar{R}|f\gamma\lambda) \tag{6-13}$$

Accordingly, we may let h represent the number of operations of the single group and include only the R operations in Eq. (6-11), and the expression for the projection operators will be identical with that for the single groups.

The result is based only on the one to one correspondence between R and $\overline{R}$ operations and the basic property (6-12), and holds independently of any choice of parameters to differentiate between them.

## C. IRREDUCIBLE REPRESENTATIONS

The irreducible representations of the point groups are given in Tables 6-3 and 6-4.

In the direct product groups $I \times G$, two representations, $\Gamma_g$ and $\Gamma_u$, correspond to every representation $\Gamma$ of the group G. The subscripts $\underline{g}$ and $\underline{u}$ indicate their symmetric or antisymmetric character, respectively, with respect to the inversion operation. The matrices for the representations $\Gamma_g$ and $\Gamma_u$ are obtained from the matrices $\Gamma(R)$ of G, according to the scheme

TABLE 6-2

| $I \times G$ | $R$ | $I \cdot R$ |
|---|---|---|
| $\Gamma_g$ | $\Gamma(R)$ | $\Gamma(R)$ |
| $\Gamma_u$ | $\Gamma(R)$ | $- \Gamma(R)$ |

The representations for the groups which are isomorphous with a group consisting only of pure rotations are taken to be the same as for the latter groups. The correspondence between the operations of two groups is easily established by the equality of the rotational factor of the operations. For example, the $\phi_k$ angles of the rotational parts of the operations of $D_{nh}$ may be written in the forms

$$\phi_k = \frac{2\pi}{2n} \; 2k$$

(6-14)

$$\phi_k + \frac{\pi}{n} = \frac{2\pi}{2n} \; (2k + 1)$$

As $\underline{k}$ assumes all integral values within its interval, Eqs. (6-2) or (6-8), the angles take all the possible values for the corresponding operations of $D_{2n}$.

The present choice of representations is such that these are completely reduced for the operations of the subgroup $C_n$ of rotations about the principal summetry axis. For these operations the representation matrices are diagonal, with elements of the form $e^{i\mu\phi_k}$. In this form it is possible to assign to every row of an irreducible representation an index, $\mu$, such that only linear combinations of angular momentum eigenfunctions with eigenvalues $\underline{m}$ of the form

$$m = \mu + np \qquad (6\text{-}15)$$

belong to that particular row. As usual, $\underline{n}$ is the multiplicity of the axis selected as z-axis, and p is an integer, positive or negative.

### C-1. CYCLIC AND DIHEDRAL GROUPS

In the case of the non-cubic point groups it is possible and convenient to assign a similar index, $\gamma$, to the irreducible representations themselves. This index may be taken as $\gamma = \mu$ or $\gamma = |\mu|$, and both are related to the possible values of $J_z$ for the eigenfunctions that belong to the corresponding representations by Eq. (6-15).

In addition to the physical meaning that can be given to $\gamma$ and $\mu$, it is possible to express the characters and matrix elements of the irreducible representations as explicit functions of these parameters. This has the further advantage that the characters and representation matrix elements for the double groups are given by the same expressions as for the single groups, by simply allowing $\gamma$ and $\mu$ to assume half-integral values within their intervals.

In what follows, all the results that shall be given for non-cubic point groups apply to the ordinary single groups for $\gamma$ and $\mu$ integral, and to the corresponding double groups for $\gamma$ and $\mu$ integral and half-integral.

The correspondence between $\gamma$ and the customary designations for the irreducible representations of these groups is straightforward, as it may be seen from the tables.

The representations characterized by $\gamma = 0$ are one-dimensional and have real characters, $\pm 1$. In particular, the characters for the rotations about the z-axis is $+1$. These representations are usually designated by the letter A.

The representations corresponding to the maximum value of $\gamma$ ($\gamma = n/2$ for $C_n$, $D_n$, and direct product groups, $\gamma = n$ for the groups isomorphous with $C_{2n}$ or $D_{2n}$) are also one-dimensional. The character for the operations involving the rotations by the smallest angle about the z-axis is $-1$. These representations are designated conventionally by the letter B.

For other integral values, $y$ corresponds to the subindex usually assigned to the doubly – degenerate E representations. Although the irreducible representations of the groups $C_n$, $S_{2n}$, and $C_{nh}$ are all one-dimensional, the pairs of complex conjugate representations are often treated as a two-dimensional representation of type E.

There is one more index required in order to differentiate between the two representations of the same type, A or B, which occur in the case of the dihedral groups. The two representations within each type are conventionally distinguished by their character, + 1 or – 1, under the two-fold rotation $R(0\pi0)$ about the y-axis. The symmetric representations are designated as $A_1$ or $B_1$, the antisymmetric ones as $A_2$ or $B_2$.

All dihedral groups have the representations $A_1$ and $A_2$. The $D_{2n}$ and related groups posses the pair $B_1$ and $B_2$, but for $\underline{n}$ odd the single groups $D_n$ do not have B-type representations.

The corresponding double groups always possess a pair of representations of type B. For the $D_{2n}$ groups these are also representations of the single group, $B_1$ and $B_2$, while in the case of $D_n$(n odd) the pair of B-type representations emerge as half-integral representations associated with $y = n/2$. In the latter case, the characters of these representations under the two-fold rotation $R(0\pi0)$ are + i or – i.

The usual notation for the non-cubic single point groups may be extended to cover the corresponding double groups with a minimum of changes by the following provisions:

a) The subindex $y$ for the $E_y$ two-dimensional representations may be allowed to assume half-integral values within its interval.

b) In the case of the **D**$_n$ and related groups the two one-dimensional representations of type B may be designated as $B_1$ and $B_2$ irrespective of whether they are integral (n even) or half-integral (n odd). In the latter case their characters under $R(0\pi0)$ are + i and – i, respectively.

The notation followed for the groups $C_{nh}$ and $D_{nh}$ for $\underline{n}$ odd is the same as for the isomorphous groups $C_{2n}$ and $D_{2n}$, respectively. The usual notation for the single groups is based on the direct product relations, $C_{1h} \times C_n$ or $C_{1h} \times D_n$, the representations being labelled by a prime or a double prime to indicate symmetric or antisymmetric character for the reflection $\sigma_h$. However, the direct product relation does not extend to the double groups $D_{nh}$. Although the direct product notation could be extended to the $C_{nh}$ double groups, it becomes unnecessarily complicated because the $C_{1h} = C_s$ double group has four irreducible representations. On the other hand the notation based on the isomorphism with $C_{2n}$ or $D_{2n}$

TABLE 6-3

*CYCLIC AND DIHEDRAL GROUPS: IRREDUCIBLE REPRESENTATIONS*

|  | $\gamma, \mu$ | $k$ | $\phi_k = \dfrac{2\pi}{n}\, k$ |
|---|---|---|---|
| Single groups | integral | $-n/2 < k \le n/2$ | $-\pi < \phi \le \pi$ |
| Double groups | integral and half-integral | $-n < k \le n$ | $-2\pi < \phi \le 2\pi$ |

| $C_n$ | $R_z(\phi_k)$ | $\mu$ |
|---|---|---|
| A | $1$ | $0$ |
| $E_\gamma$ $(0<\gamma<n/2)$ | $\begin{cases} e^{i\gamma\phi_k} \\[4pt] e^{-i\gamma\phi_k} \end{cases}$ | $\gamma$ <br> $-\gamma$ |
| B | $(-1)^k$ | $n/2$ |

| (n even) $S_{2n}$ (n odd) $C_{nh}$ | $R_z(\phi_k)$ | $I \cdot R_z\!\left(\phi_k + \dfrac{\pi}{n}\right)$ | $\mu$ |
|---|---|---|---|
| A | $1$ | $1$ | $0$ |
| $E_\gamma$ $(0<\gamma<n)$ | $\begin{cases} e^{i\gamma\phi_k} \\[4pt] e^{-i\gamma\phi_k} \end{cases}$ | $\begin{cases} e^{i\gamma(\phi_k+\frac{\pi}{n})} \\[4pt] e^{-i\gamma(\phi_k+\frac{\pi}{n})} \end{cases}$ | $\gamma$ <br> $-\gamma$ |
| B | $1$ | $-1$ | $n$ |

$$\left.\begin{array}{l}(\text{n odd})\quad S_{2n} \\[6pt] (\text{n even})\quad C_{nh}\end{array}\right\} = I \times C_n$$

| $D_n$ | $R_z(\phi_k)$ | $R(\phi_k, \pi)$ | $\mu$ |
|---|---|---|---|
| $C_{nv}$ | $R_z(\phi_k)$ | $I \cdot R(\phi_k, \pi)$ | |
| $A_1$ | $1$ | $1$ | $0$ |
| $A_2$ | $1$ | $-1$ | $0$ |
| $E_\gamma$ $(0<\gamma<n/2)$ | $\begin{bmatrix} e^{i\gamma\phi_k} & 0 \\ 0 & e^{-i\gamma\phi_k} \end{bmatrix}$ | $\begin{bmatrix} 0 & e^{i\gamma\phi_k} \\ (-1)^{2\gamma}e^{-i\gamma\phi_k} & 0 \end{bmatrix}$ | $\gamma$ <br> $-\gamma$ |
| n even $\begin{cases} B_1 \\ B_2 \end{cases}$ | $(-1)^k$ <br> $(-1)^k$ | $(-1)^k$ <br> $-(-1)^k$ | $n/2$ <br> $n/2$ |
| n odd $\begin{cases} B_1 \\ B_2 \end{cases}$ | $(-1)^k$ <br> $(-1)^k$ | $i(-1)^k$ <br> $-i(-1)^k$ | $n/2$ <br> $n/2$ |

Table 6-3 (Continued)

| (n even) $\mathbf{D}_{nd}$ (n odd) $\mathbf{D}_{nh}$ | $R_z(\phi_k)$ | $R(\phi_k, \pi)$ | $I \cdot R_z(\phi_k + \frac{\pi}{n})$ | $I \cdot R(\phi_k + \frac{\pi}{n}, \pi)$ | $\mu$ |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 0 |
| $A_2$ | 1 | $-1$ | 1 | $-1$ | 0 |
| $E_\gamma$ $(0<\gamma<n)$ | $\begin{bmatrix} e^{i\gamma\phi_k} & 0 \\ 0 & e^{-i\gamma\phi_k} \end{bmatrix}$ | $\begin{bmatrix} 0 & e^{i\gamma\phi_k} \\ (-1)^{2\gamma}e^{-i\gamma\phi_k} & 0 \end{bmatrix}$ | $\begin{bmatrix} e^{i\gamma(\phi_k+\frac{\pi}{n})} & 0 \\ 0 & e^{-i\gamma(\phi_k+\frac{\pi}{n})} \end{bmatrix}$ | $\begin{bmatrix} 0 & e^{i\gamma(\phi_k+\frac{\pi}{n})} \\ (-1)^{2\gamma}e^{-i\gamma(\phi_k+\frac{\pi}{n})} & 0 \end{bmatrix}$ | $\gamma$ $-\gamma$ |
| $B_1$ | 1 | 1 | $-1$ | $-1$ | n |
| $B_2$ | 1 | $-1$ | $-1$ | 1 | n |

(n odd) $\mathbf{D}_{nd}$

(n even) $\mathbf{D}_{nh}$  $\Big\}$ $= I \times \mathbf{D}_n$

is simpler, easily extended to the double groups, and more in line with that of the other non-cubic groups. The correspondence between this and the usual notation for the representations of the single groups is easily established, as follows: for $\gamma$ even, the present $E_\gamma$ corresponds to $E'_{\gamma/2}$, while for $\gamma$ odd the complex conjugate of the present $E_{(n-\gamma)}$ corresponds to $E''_{\gamma/2}$.

### C-2. CUBIC GROUPS

The operations of the cubic groups have been specified in Table 6-1 in a rather general form, by the conditions to be satisfied by the sum $\alpha + \beta + \gamma$ of the Eulerian angles (referred to the usual cubic set of axes). It may be easily seen that, for example, the condition $\alpha + \beta + \gamma = k\pi$, ($k$ = integer) is satisfied by the Eulerian angles of twelve non-equivalent rotations

$$\beta = 0 \qquad \alpha + \gamma = 0, \pi$$
$$\beta = \pi \qquad \alpha - \gamma = 0, \pi$$

$$\beta = \frac{\pi}{2} \begin{cases} \alpha = 0, \pi \qquad \gamma = \frac{\pi}{2}, -\frac{\pi}{2} \\ \\ \alpha = \frac{\pi}{2}, -\frac{\pi}{2} \qquad \gamma = 0, \pi \end{cases}$$

(6-16)

The individual operations of the groups T and O are listed in Table 6-5. The corresponding transformations of the coordinate system are indicated in Fig. 6-1.

The operations of the remaining groups, $T_d$, $T_h$, and $O_h$, may be obtained from these without difficulty.

The tables of characters for the cubic groups are given in Table 6-6. They are given for only half of the operations of the double groups. The Eulerian angles listed under the class headings have been taken according to the convention of Section 6, Eqs. (6-3) and (6-4). The number of operations in the classes containing two-fold rotations $R(\alpha \pi \gamma)$ are given as fractions as a reminder of the fact that in the double groups the corresponding $\bar{R}$ operations do not form new classes.

The irreducible representations of the group O in terms of the Eulerian angles are given in Table 6-4. These are also the representations for the isomorphous group $T_d$.

The matrices of the representations of O for the operations of its subgroup T afford the irreducible representations for T. Our choice is such that conjugate representations in O have identical matrices for the subgroup T. Thus, for example, the matrices for $F_1$ and $F_2$ of O give the same matrices for the F representation of T. Similarly, the matrices of the representations $E_{1/2}$ or $E_{5/2}$ of O afford the representation $E_{1/2}$ of T.

The representation matrices for the self-conjugate representations, E and $G_{3/2}$, of O in the form given afford representations of T which are not in reduced form. The reason for this choice is to avoid the presence of complex coefficients in the expressions for the symmetry functions. These representation matrices may be brought to reduced form unuer T by a unitary transformation, Eq. (3-5), by means of the matrices

$$A^{(E)} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ i/\sqrt{2} & -i/\sqrt{2} \end{pmatrix} \tag{6-17}$$

$$A^{(G3/2)} = \begin{pmatrix} 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} \\ 0 & -i/\sqrt{2} & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & 0 & -i/\sqrt{2} \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \end{pmatrix} \tag{6-18}$$

The representation matrices for the direct product groups $T_h$ and $O_h$ may be obtained by the usual rule (Table 6-2).

## IRREDUCIBLE REPRESENTATIONS OF THE GROUP O
### INTEGRAL REPRESENTATIONS (CUBIC AXES)

| $\Gamma$ | $\Gamma(\alpha, \beta, \gamma)$ |
|---|---|
| $A_1$ | $1$ |
| $A_2$ | $\cos 2(\pm\alpha \pm \beta \pm \gamma)$ |

$$E \quad \begin{bmatrix} \frac{1}{2}(3\cos^2\beta - 1) & \frac{\sqrt{3}}{2}\sin^2\beta \cos 2\gamma \\[2ex] \frac{\sqrt{3}}{2}\sin^2\beta \cos 2\alpha & \frac{1}{2}(1 + \cos^2\beta)\sin 2\alpha \sin 2\gamma \end{bmatrix}$$

$$F_1 \quad \begin{bmatrix} \frac{1}{2}(1 + \cos\beta)e^{i(\alpha+\gamma)} & \frac{1}{\sqrt{2}}\sin\beta\, e^{i\alpha} & \frac{1}{2}(1 - \cos\beta)e^{i(\alpha-\gamma)} \\[2ex] -\frac{1}{\sqrt{2}}\sin\beta\, e^{i\gamma} & \cos\beta & \frac{1}{\sqrt{2}}\sin\beta\, e^{-i\gamma} \\[2ex] \frac{1}{2}(1 - \cos\beta)e^{-i(\alpha-\gamma)} & -\frac{1}{\sqrt{2}}\sin\beta\, e^{-i\alpha} & \frac{1}{2}(1 + \cos\beta)e^{-i(\alpha+\gamma)} \end{bmatrix}$$

$$F_2 \quad \Gamma^{A_2} \times \Gamma^{F_1}$$

TABLE 6-4 (Continued)

## IRREDUCIBLE REPRESENTATIONS OF THE GROUP O
## HALF-INTEGRAL REPRESENTATIONS

| $\Gamma$ | $\Gamma(\alpha, \beta, \gamma)$ |
|---|---|

$E_{1/2}$

$$\begin{bmatrix} e^{\frac{1}{2}(\alpha+\gamma)} \cos\frac{\beta}{2} & e^{\frac{1}{2}(\alpha-\gamma)} \sin\frac{\beta}{2} \\ -e^{-\frac{1}{2}(\alpha-\gamma)} \sin\frac{\beta}{2} & e^{-\frac{1}{2}(\alpha+\gamma)} \cos\frac{\beta}{2} \end{bmatrix}$$

$E_{5/2}$

$$\Gamma^{A_2} \times \Gamma^{E_{1/2}}$$

$G_{3/2}$

$$\begin{bmatrix} e^{i(\frac{3}{2}\alpha+\frac{3}{2}\gamma)} c^3 & e^{i(\frac{3}{2}\alpha+\frac{1}{2}\gamma)}\sqrt{3}c^2s & e^{i(\frac{3}{2}\alpha-\frac{1}{2}\gamma)}\sqrt{3}cs^2 & e^{i(\frac{3}{2}\alpha-\frac{3}{2}\gamma)}s^2 \\ -e^{i(\frac{1}{2}\alpha+\frac{3}{2}\gamma)}\sqrt{3}c^2s & e^{i(\frac{1}{2}\alpha+\frac{1}{2}\gamma)}(c^3-2cs^2) & e^{i(\frac{1}{2}\alpha-\frac{1}{2}\gamma)}(-s^3+2sc^2) & e^{i(\frac{1}{2}\alpha-\frac{3}{2}\gamma)}\sqrt{3}cs^2 \\ e^{i(-\frac{1}{2}\alpha+\frac{3}{2}\gamma)}\sqrt{3}cs^2 & e^{i(-\frac{1}{2}\alpha+\frac{1}{2}\gamma)}(s^3-2sc^2) & e^{i(-\frac{1}{2}\alpha-\frac{1}{2}\gamma)}(c^3-2s^2c) & e^{i(-\frac{1}{2}\alpha-\frac{3}{2}\gamma)}\sqrt{3}c^2s \\ -e^{i(-\frac{3}{2}\alpha+\frac{3}{2}\gamma)}s^3 & e^{i(-\frac{3}{2}\alpha+\frac{1}{2}\gamma)}\sqrt{3}cs^2 & -e^{i(-\frac{3}{2}\alpha-\frac{1}{2}\gamma)}\sqrt{3}c^2s & e^{i(-\frac{3}{2}\alpha-\frac{3}{2}\gamma)}c^3 \end{bmatrix}$$

$$c = \cos\frac{\beta}{2}, \quad s = \sin\frac{\beta}{2}$$

TABLE 6-5

GROUP O   *Eulerian Angles (Cubic Axes)*

| SUBGROUP T | | COSET T·$C_2'$ | |
|---|---|---|---|
| R | $(\gamma,\beta,a)$ | R $C_2'$ | $(\gamma,\beta,a)$ |
| E | $(0,0,0)$ | $C_2'(xy)$ | $(0,\pi,\frac{\pi}{2})$ |
| $C_2(z)$ | $(\pi,0,0)$ | $C_2'(-xy)$ | $(0,\pi,-\frac{\pi}{2})$ |
| $C_2(y)$ | $(0,\pi,0)$ | $C_4(z)$ | $(\frac{\pi}{2},0,0)$ |
| $C_2(x)$ | $(0,\pi,\pi)$ | $C_4^{-1}(z)$ | $(-\frac{\pi}{2},0,0)$ |
| $C_3(1,1,1)$ | $(0,\frac{\pi}{2},\frac{\pi}{2})$ | $C_4^{-1}(y)$ | $(\pi,\frac{\pi}{2},\pi)$ |
| $C_3(-1,1,-1)$ | $(0,\frac{\pi}{2},-\frac{\pi}{2})$ | $C_2'(-xz)$ | $(\pi,\frac{\pi}{2},0)$ |
| $C_3(1,-1,-1)$ | $(\pi,\frac{\pi}{2},\frac{\pi}{2})$ | $C_2'(xz)$ | $(0,\frac{\pi}{2},\pi)$ |
| $C_3(-1,-1,1)$ | $(\pi,\frac{\pi}{2},-\frac{\pi}{2})$ | $C_4(y)$ | $(0,\frac{\pi}{2},0)$ |
| $C_3^{-1}(1,1,1)$ | $(\frac{\pi}{2},\frac{\pi}{2},\pi)$ | $C_4(x)$ | $(-\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2})$ |
| $C_3^{-1}(-1,1,-1)$ | $(-\frac{\pi}{2},\frac{\pi}{2},\pi)$ | $C_2'(yz)$ | $(\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2})$ |
| $C_3^{-1}(1,-1,-1)$ | $(\frac{\pi}{2},\frac{\pi}{2},0)$ | $C_2'(-yz)$ | $(-\frac{\pi}{2},\frac{\pi}{2},-\frac{\pi}{2})$ |
| $C_3^{-1}(-1,-1,1)$ | $(-\frac{\pi}{2},\frac{\pi}{2},0)$ | $C_4^{-1}(x)$ | $(\frac{\pi}{2},\frac{\pi}{2},-\frac{\pi}{2})$ |

TABLE 6-6

CHARACTER TABLES FOR THE CUBIC GROUPS

| T | E | $\frac{6}{2}C_2$ | $4C_3$ | $4C_3^{-1}$ | |
|---|---|---|---|---|---|
| $(\gamma, \beta, a)$ | $(0,0,0)$ | $(\pi,0,0)$ $(0,\pi,0)$ $(\pi,\pi,0)$ | $(0,\pm\frac{\pi}{2},\pm\frac{\pi}{2})$ | $(\pm\frac{\pi}{2},\pm\frac{\pi}{2},0)$ | |
| A | 1 | 1 | 1 | 1 | |
| E $\{$ | 1 / 1 | 1 / 1 | $\epsilon$ / $\epsilon^{-1}$ | $\epsilon^{-1}$ / $\epsilon$ | $\epsilon = e^{i\frac{2\pi}{3}}$ |
| F | 3 | $-1$ | 0 | 0 | |
| $E_{1/2}$ | 2 | 0 | 1 | 1 | |
| $G_{3/2}$ $\{$ | 2 / 2 | 0 / 0 | $\epsilon$ / $\epsilon^{-1}$ | $\epsilon^{-1}$ / $\epsilon$ | |

Integral: A, E, F
Half-integral: $E_{1/2}$, $G_{3/2}$
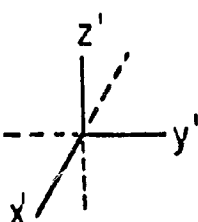
| $T_d$ / $O$ | E / E | $\frac{6}{2}C_2$ / $\frac{6}{2}C_2$ | $8C_3$ / $8C_3$ | $6S_4$ / $6C_4$ | $\frac{12}{2}\sigma_d$ / $\frac{12}{2}C_2'$ |
|---|---|---|---|---|---|
| $(\gamma,\beta,a)$ | $(0,0,0)$ | $(\pi,0,0)$ $(0,\pi,0)$ $(\pi,\pi,0)$ | $(0,\pm\frac{\pi}{2},\pm\frac{\pi}{2})$ $(\pm\frac{\pi}{2},\pm\frac{\pi}{2},0)$ | $(\pm\frac{\pi}{2},0,0)$ $(0,\pm\frac{\pi}{2},0)$ $(\frac{\pi}{2},\pm\frac{\pi}{2},-\frac{\pi}{2})$ | $(0,\pi,\pm\frac{\pi}{2})$ $(\pi,\pm\frac{\pi}{2},0)$ $(\frac{\pi}{2},\pm\frac{\pi}{2},\frac{\pi}{2})$ |
| $A_1$ | 1 | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | 1 | $-1$ | $-1$ |
| E | 2 | 2 | $-1$ | 0 | 0 |
| $F_1$ | 3 | $-1$ | 0 | 1 | $-1$ |
| $F_2$ | 3 | $-1$ | 0 | $-1$ | 1 |
| $E_{1/2}$ | 2 | 0 | 1 | $\sqrt{2}$ | 0 |
| $E_{5/2}$ | 2 | 0 | 1 | $-\sqrt{2}$ | 0 |
| $G_{3/2}$ | 4 | 0 | $-1$ | 0 | 0 |

Integral: $A_1$, $A_2$, E, $F_1$, $F_2$
Half-integral: $E_{1/2}$, $E_{5/2}$, $G_{3/2}$
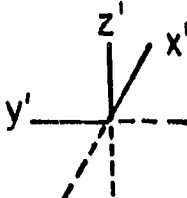
$$T_h = I \times T$$
$$O_h = I \times O$$

# CUBIC GROUP O: SYMMETRY OPERATIONS
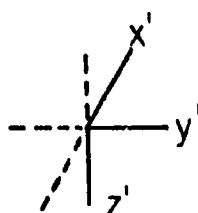
E
(0,0,0)
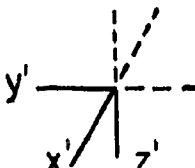
$C_2(z)$
$(\pi,0,0)$
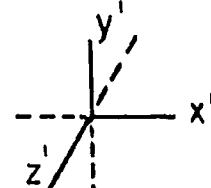
$C_2(y)$
$(0,\pi,0)$
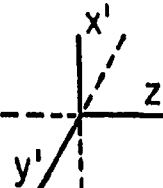
$C_2(x)$
$(0,\pi,\pi)$
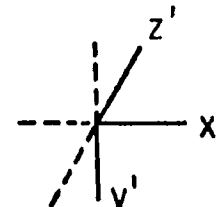
$C_3(1,1,1)$
$(0,\frac{\pi}{2},\frac{\pi}{2})$
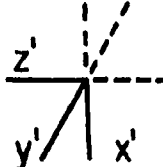
$C_3^{-1}(1,1,1)$
$(\frac{\pi}{2},\frac{\pi}{2},\pi)$
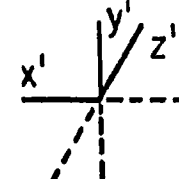
$C_3(-1,-1,1)$
$(\pi,\frac{\pi}{2},-\frac{\pi}{2})$
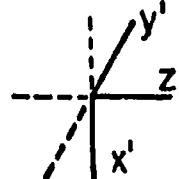
$C_3^{-1}(-1,-1,1)$
$(-\frac{\pi}{2},\frac{\pi}{2},0)$
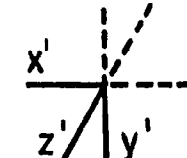
$C_3(1,-1,-1)$
$(\pi,\frac{\pi}{2},\frac{\pi}{2})$
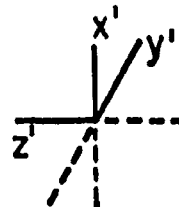
$C_3^{-1}(1,-1,-1)$
$(\frac{\pi}{2},\frac{\pi}{2},0)$

$C_3(-1,1,-1)$
$(0,\frac{\pi}{2},-\frac{\pi}{2})$

$C_3^{-1}(-1,1,-1)$
$(-\frac{\pi}{2},\frac{\pi}{2},\pi)$

$C_4(z)$
$(\frac{\pi}{2},0,0)$
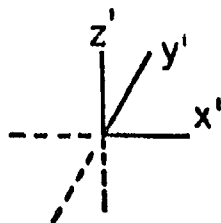
$C_4^{-1}(z)$
$(-\frac{\pi}{2},0,0)$
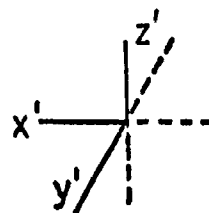
$C_4(x)$
$(-\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2})$
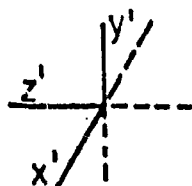
$C_4^{-1}(x)$
$(\frac{\pi}{2},\frac{\pi}{2},-\frac{\pi}{2})$
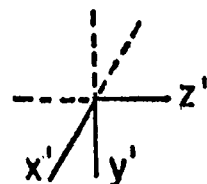
$C_4(y)$
$(0,\frac{\pi}{2},0)$
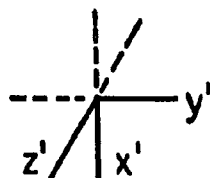
$C_4^{-1}(y)$
$(\pi,\frac{\pi}{2},\pi)$
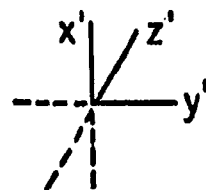
$C_2'(xy)$
$(0,\pi,\frac{\pi}{2})$
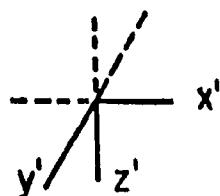
$C_2'(-xy)$
$(0,\pi,-\frac{\pi}{2})$
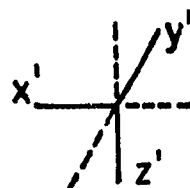
$C_2'(yz)$
$(\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2})$
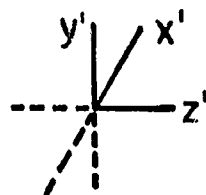
$C_2'(-yz)$
$(-\frac{\pi}{2},\frac{\pi}{2},-\frac{\pi}{2})$
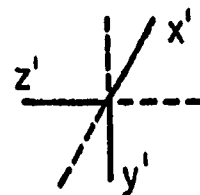
$C_2'(xz)$
$(0,\frac{\pi}{2},\pi)$
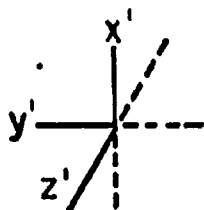
$C_2'(-xz)$
$(\pi,\frac{\pi}{2},0)$
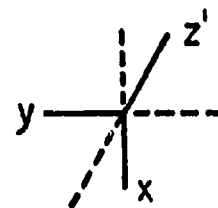
# GROUP O: REDUCTION OF THE REPRESENTATIONS $\Gamma_j$

| j | IRREDUCIBLE REPRESENTATIONS | | | | |
|---|---|---|---|---|---|
| 0 | $A_1$ | | | | |
| 1 | | | | $F_1$ | |
| 2 | | | $E$ | | $F_2$ |
| 3 | | $A_2$ | | $F_1$ | $F_2$ |
| 4 | $A_1$ | | $E$ | $F_1$ | $F_2$ |
| 5 | | | $E$ | $2F_1$ | $F_2$ |
| 6 | $A_1$ | $A_2$ | $E$ | $F_1$ | $2F_2$ |
| 7 | | $A_2$ | $E$ | $2F_1$ | $2F_2$ |
| 8 | $A_1$ | | $2E$ | $2F_1$ | $2F_2$ |
| 9 | $A_1$ | $A_2$ | $E$ | $3F_1$ | $2F_2$ |
| 10 | $A_1$ | $A_2$ | $2E$ | $2F_1$ | $3F_2$ |
| 11 | | $A_2$ | $2E$ | $3F_1$ | $3F_2$ |
| 12 | $2A_1$ | $A_2$ | $2E$ | $3F_1$ | $3F_2$ |
| $\Gamma_{reg.}$ | $A_1$ | $A_2$ | $2E$ | $3F_1$ | $3F_2$ |

$$\Gamma_{12n+j} = n\,\Gamma_{reg.} + \Gamma_j$$

| j | IRREDUCIBLE REPRESENTATIONS | | |
|---|---|---|---|
| 1/2 | $E_{1/2}$ | | |
| 3/2 | | | $G_{3/2}$ |
| 5/2 | | $E_{5/2}$ | $G_{3/2}$ |
| 7/2 | $E_{1/2}$ | $E_{5/2}$ | $G_{3/2}$ |
| 9/2 | $E_{1/2}$ | | $2G_{3/2}$ |
| 11/2 | $E_{1/2}$ | $E_{5/2}$ | $2G_{3/2}$ |
| 13/2 | $E_{1/2}$ | $2E_{5/2}$ | $2G_{3/2}$ |
| 15/2 | $E_{1/2}$ | $E_{5/2}$ | $3G_{3/2}$ |
| 17/2 | $2E_{1/2}$ | $E_{5/2}$ | $3G_{3/2}$ |
| 19/2 | $2E_{1/2}$ | $2E_{5/2}$ | $3G_{3/2}$ |
| 21/2 | $E_{1/2}$ | $2E_{5/2}$ | $4G_{3/2}$ |
| 23/2 | $2E_{1/2}$ | $2E_{5/2}$ | $4G_{3/2}$ |
| 25/2 | $3E_{1/2}$ | $2E_{5/2}$ | $4G_{3/2}$ |

$$\Gamma_{12n+j} = 2n\,\Gamma_{11/2} + \Gamma_j$$

# 7. SYMMETRY FUNCTIONS

The transformation properties of the angular momentum eigenfunctions under rotations have already been considered in Section 5. It may be mentioned that the transformation co-efficients depend only on the eigenvalues $j$ and $\underline{m}$, and they are independent of the kind of angular momentum, whether orbital or spin, of the number of particles in the system, etc.

This is no longer true when the transformation properties under inversion are considered. The spin eigenfunctions are invariant under inversion, but the orbital angular momentum eigenfunctions of a particle transform as the spherical harmonics, that is

$$I \mid \ell m) = (-1)^{\ell} \mid \ell m) \tag{7-1}$$

As the angular momentum eigenfunctions in atomic or molecular problems are linear combinations of product functions of several particles, each with a certain value of $\ell$, the product functions transform as

$$I \mid \ell_1 m_1) \mid \ell_2 m_2) \ldots \mid \ell_i m_i) \ldots = (-1)^{\sum_i \ell_i} \mid \ell_1 m_1) \mid \ell_2 m_2) \ldots \mid \ell_i m_i) \ldots \tag{7-2}$$

Accordingly the functions will be symmetric or antisymmetric with respect to the inversion according as to whether the sum $\sum_i \ell_i$ of the orbital quantum numbers is even or odd. The even or odd parity of functions may be represented by an index $\sigma$ which can take the values 0 or 1, respectively, and we may write in general

$$I \mid \sigma j m) = (-1)^{\sigma} \mid \sigma j m) \tag{7-3}$$

In what follows we may always assume that the angular momentum eigenfunctions under consideration have a definite parity, specified by the quantum number $\sigma$.

We shall now proceed to determine the general expressions for the linear combinations of angular momentum eigenfunctions that belong to the different irreducible representations of the point groups. For each representation of dimension $\underline{d}$ they form sets of $\underline{d}$ partners, each characterized by a different value of the index $\mu$, that labels the rows of the representation. In general, the operations of the group transform any of the partners into a linear combination of all of them as in Eq. (3-10).

$$R \mid f \sigma \gamma \mu') = \sum_{\mu} \mid f \sigma \gamma \mu) (\sigma \gamma \mu \mid R \mid \sigma \gamma \mu') \qquad (7\text{-}4)$$

The indices $\mu, \mu'$ label the rows and columns of the irreducible representation, the indices $\sigma$ and $\gamma$ label the representations themselves, and the index $\underline{f}$ stands for all the remaining labels or quantum numbers specifying the function and which are not affected by the group operations, and will be omitted unless necessary.

For the simplest groups, the symmetry functions formed from the $\mid \sigma j m)$ eigenfunctions may be found by inspection but in general the use of the projection operators leads to the desired results in a simple form.

The expression for the projection operators (Eq. 4-14) to be used is

$$P^{(\gamma\sigma)}_{\mu\mu'} = \frac{d}{h} \sum_{R} (\sigma \gamma \mu \mid R \mid \sigma \gamma \mu')^* R \qquad (7\text{-}5)$$

As indicated in Section 4, if the original set of functions whose symmetry linear combinations are to be determined afford a representation (reducible or irreducible) of the group, all the possible sets of symmetry functions for a given irreducible representation may be obtained by using only the operators associated with any particular column of the irreducible representation. In our case, the $\mid \sigma j m)$ basis functions associated with given values of $\sigma$ and $\underline{j}$, and all the corresponding values of $\underline{m}$ from $-j$ to $\underline{j}$, afford a representation of the group. Moreover, with our choice of representations, all the symmetry functions belonging to the $\mu$-th row of a representation must be linear combinations of $\mid \sigma j m)$ functions with the possible values of $\underline{m}$ given by Eq. (6-15)

$$m = \mu + np \qquad (7\text{-}6)$$

These functions are all different from those corresponding to another row $\mu'$ (since the difference $\mu' - \mu$ is never zero or multiple of $\underline{n}$).

Conversely, even when the $\mid \sigma j m)$ functions of the family defined by $\underline{m} = \mu + \underline{n}p$ are not themselves symmetry functions, they never contain symmetry functions belonging to a different row $\mu'$ of the same irreducible representation.

According to Eq. (4-9) the projection operators associated with the column $\mu$ of an irreducible representation give a non-vanishing result only when they operate on functions that contain symmetry functions belonging to the $\mu$-th row.

7-2

If follows that in order to obtain all the symmetry functions that belong to a certain representation it is sufficient to apply the projection operators associated with any fixed column $\mu$ to the $|\sigma j m)$ functions with $\underline{m} = \mu + \underline{n}p$. When applied to the same $|\sigma j m)$, they generate a set of partner functions, each belonging to the row $\mu'$ of the corresponding operator, $P_{\mu'\mu}^{(\gamma)}$.

For example, in the case of the non-cubic point groups the highest dimension of the irreducible representations is $\underline{d} = 2$, and the values of the indices $\mu$ and $\mu'$ labeling the rows and columns of the representation $E_\gamma$ are $\gamma$ and $-\gamma$. The operators to be considered are

$$\begin{bmatrix} P_{\gamma,\gamma}^{(\gamma)} & P_{\gamma,-\gamma}^{(\gamma)} \\ \\ P_{-\gamma,\gamma}^{(\gamma)} & P_{-\gamma,-\gamma}^{(\gamma)} \end{bmatrix} \tag{7-7}$$

The operators $P_{\gamma,\gamma}^{(\gamma)}$ and $P_{-\gamma,\gamma}^{(\gamma)}$ give a non-vanishing result only when they operate on functions which belong to the first row or contain such functions. With our choice of representations, the first row functions are characterized by eigenvalues $\underline{m}$ of the form $\underline{m} = \gamma + \underline{n}p$, while for their second row partners $\underline{m} = -\gamma - \underline{n}p$.

The operator $P_{\gamma,\gamma}^{(\gamma)}$ generates the first row partner and the operator $P_{-\gamma,\gamma}^{(\gamma)}$ the second row partner when operating on the same first row function. All the independent pairs of basis functions are obtained by the action of these operators on the $|\sigma j m)$ basis functions with $\underline{m} = \gamma + \underline{n}p$. The functions obtained are all independent and orthogonal to each other, and no redundancy problems arise.

In the case of the non-degenerate representations $A_1$, $A_2$, $B_1$, and $B_2$, the symmetry functions are of the forms

$$|\sigma j m) \pm |\sigma j, -m)$$

and it is only necessary to operate on the functions with $\underline{m} \geq 0$. The functions with negative values of $\underline{m}$ yield symmetry functions differing from the previous ones only by a constant factor.

The redundancy and non-orthogonality problems arising for some representations of the cubic groups are slightly more complicated. They shall be consider later.

7-3

## A. NON CUBIC GROUPS

In addition to Eq. (7-5), we shall need the following expressions for the transformation of the $|\sigma j m)$ functions

$$R_z(\phi) \, |\sigma j m) = |\sigma j m) \, e^{im\phi} \tag{7-8}$$

$$R(\phi,\pi) \, |\sigma j m) = (-1)^{j+m} |\sigma j, -m) \, e^{-im\phi} \tag{7-9}$$

$$I \, |\sigma j m) = (-1)^{\sigma} \, |\sigma j m) \tag{7-10}$$

We shall also make frequent use of the familiar summation formula

$$\sum_{k=0}^{n-1} e^{i \frac{2\pi}{n} k\lambda} = n \cdot \delta(\lambda, np) \tag{7-11}$$

where $\underline{p}$ is an integer, positive or negative, and $\delta(\lambda,np)$ is the familiar delta function

$$\delta(\lambda,np) = \begin{cases} 1 & \text{for } \lambda = np \\ 0 & \text{for } \lambda \neq np \end{cases} \tag{7-12}$$

*Groups* $\mathbf{C}_n$

Since the representations are one-dimensional with characters

$$\chi^{(\mu)}(\phi_k) = e^{i\mu\phi_k} \tag{7-13}$$

the effect of the projection operators on the $|\sigma j m)$ eigenfunctions is

$$P^{(\mu)} \, |\sigma j m) = \frac{1}{n} \sum_k |\sigma j m) \, e^{i(m-\mu)\frac{2\pi}{n}k} = |\sigma j m) \, \delta(m, \mu + np) \tag{7-14}$$

The functions $|\sigma j m)$ and $|\sigma j, -m)$ belong to complex conjugate representations. Although these are often considered as a two-dimensional representation $E_\gamma, (\gamma = |\mu|)$, it should be kept in mind that the pairs of functions are not "partners," since they never transform into each other under the group operations. These remarks apply also to the $S_{2n}$ and $C_{nh}$ groups.

*Groups $S_{2n}$ (n odd) and $C_{nh}$ (n even)*

Since these are the direct product groups $1 \times C_n$, the effect of the projection operators on the $|\sigma j m)$ eigenfunctions is as follows

$$P^{(\mu g)}|\sigma j m) = |\sigma j m) \, \delta(\sigma,0) \, \delta(m,\mu+np)$$

$$P^{(\mu u)}|\sigma j m) = |\sigma j m) \, \delta(\sigma,1) \, \delta(m,\mu+np)$$

(7-15)

so that the functions with eigenvalues $\underline{m} = \mu + \underline{np}$ belong to the representation $y\underline{g}$ or $y\underline{u}$ according as to whether their parity is even or odd, respectively.

*Groups $S_{2n}$ (n even) and $C_{nh}$ (n odd)*

These groups are isomorphous with the corresponding $C_{2n}$. The symmetry functions are

$$P^{(\mu)}|\sigma j m) = |\sigma j m) \, \frac{1}{2n} \, \sum_k e^{i(m-\mu)\phi_k} + (-1)^\sigma \, e^{i(m-\mu)(\phi_k + \frac{\pi}{n})}$$

(7-16)

If the angles $\phi_k$ are expressed as in Eq. (6-14) and consider that we can also write

$$(-1)^\sigma = e^{-i \frac{2\pi}{2n} n\sigma(2k+1)}$$

(7-17)

we obtain

$$P^{(\mu)}|\sigma j m) = |\sigma j m) \, \frac{1}{2n} \, \sum e^{i(m-\mu-n\sigma)\frac{2\pi}{2n} 2k} + e^{i(m-\mu-n\sigma)\frac{2\pi}{2n}(2k+1)} = |\sigma j m) \, \delta(m,\mu+n\sigma+2np)$$ (7-18)

As indicated previously, for $y = |\mu|$ even, the representations designated here as $E_y$ correspond to the representations of the single group $C_{nh}$ usually designated as $E'_{y/2}$, while for $y$ odd, the complex conjugate of $E_{n-y}$ corresponds to the usual $E''_{y/2}$. It may be noticed that for given integral $j\underline{m}$, if a function of a certain parity belongs to an $E'$ representation, the corresponding function of opposite parity will belong to an $E''$ representation.

*Groups $D_n$*

Unlike the groups considered thus far, the dihedral groups contain symmetry operations involving rotations about axes perpendicular to the principal symmetry axis. The projection operators are no longer diagonal in $\underline{m}$, and when acting on the $|\sigma j m)$ eigenfunctions generate linear combinations of $|\sigma j m)$ and $|\sigma j,-m)$, as follows;

$$\sqrt{2}\ P^{(A\,1)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) + (-1)^{j+m}|\sigma j,-m)\}\ \delta(m,np)$$

$$\sqrt{2}\ P^{(A\,2)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) - (-1)^{j+m}|\sigma j,-m)\}\ \delta(m,np) \tag{7-19}$$

$$\begin{cases} P^{(\gamma)}_{\gamma,\gamma}\ |\sigma j\,m) = |\sigma j\,m)\ \delta(m,\gamma+np) \\[2mm] P^{(\gamma)}_{-\gamma,\gamma}\ |\sigma j\,m) = (-1)^{j+m+2\gamma}\ |\sigma j,-m)\ \delta(m,\gamma+np) \end{cases} \tag{7-20}$$

For $\underline{n}$ even, the representations $B_1$ and $B_2$ are integral, and we have

$$\cdot\quad \sqrt{2}\ P^{(B\,1)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) + (-1)^{j+m}|\sigma j,-m)\}\ \delta(m,\tfrac{n}{2}+np)$$

$$\sqrt{2}\ P^{(B\,2)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) - (-1)^{j+m}|\sigma j,-m)\}\ \delta(m,\tfrac{n}{2}+np) \tag{7-21}$$

For $\underline{n}$ odd, the representations $B_1$ and $B_2$ are half integral, and the functions that belong to those representations are of the form

$$\sqrt{2}\ P^{(B\,2)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) + i\,(-1)^{j+m}|\sigma j,-m)\}\ \delta(m,\tfrac{n}{2}+np)$$

$$\sqrt{2}\ P^{(B\,1)}\ |\sigma jm) = \sqrt{\tfrac{1}{2}}\ \{|\sigma j\,m) - i\,(-1)^{j+m}|\sigma j,-m)\}\ \delta(m,\tfrac{n}{2}+np) \tag{7-22}$$

It may be noticed that the average value of $J_z$ in the non-degenerate states is always zero.

## Groups $C_{nv}$

These groups are isomorphous with $D_n$. The presence of the operations $I \cdot R(\phi_k,\pi)$ introduces a factor $(-1)^\sigma$ in the transformation coefficients which apply to the corresponding operations $R(\phi_k,\pi)$ of $D_n$. The expressions for the symmetry functions may be obtained from those for $D_n$ if the factor $(-1)^{j+m}$ in the coefficients of $|\sigma j,-m)$ is replaced by $(-1)^{j+m+\sigma}$.

*Groups $D_{nd}$ (n odd) and $D_{nh}$ (n even)*

These groups are the direct products $I \times D_n$. Functions that belong to a given representation of the subgroup $D_n$ belong to the corresponding g or u representation of these groups, depending on whether they have even or odd parity, respectively.

*Groups $D_{nd}$ (n even) and $D_{nh}$ (n odd)*

These are isomorphous with the corresponding groups $D_{2n}$. Proceeding in a similar form as for the groups $S_{2n}$ (n even) and $C_{nh}$ (n odd), the following expressions for the symmetry functions are obtained

$$\sqrt{2} \; P^{(A1)} |\sigma jm) = \sqrt{\tfrac{1}{2}} \; \{|\sigma j m) + (-1)^{j+m} |\sigma j, -m)\} \; \delta(m, n\sigma + 2np)$$

$$\sqrt{2} \; P^{(A2)} |\sigma jm) = \sqrt{\tfrac{1}{2}} \; \{|\sigma j m) - (-1)^{j+m} |\sigma j, -m)\} \; \delta(m, n\sigma + 2np)$$

(7-23)

$$\begin{cases} P^{(\gamma)}_{\gamma, \gamma} \; |\sigma j m) & = \; |\sigma j m) \; \delta(m, \gamma + n\sigma + 2np) \\ \\ P^{(\gamma)}_{-\gamma, \gamma} \; |\sigma j m) & = \; (-1)^{j+m+2\gamma} \; |\sigma j, -m) \; \delta(m, \gamma + n\sigma + 2np) \end{cases}$$

(7-24)

and, since the representations $B_1$ and $B_2$ for these groups are integral

$$\sqrt{2} \; P^{(B1)} |\sigma jm) = \sqrt{\tfrac{1}{2}} \; \{|\sigma j m) + (-1)^{j+m} |\sigma j, -m)\} \; \delta(m, n + n\sigma + 2np)$$

$$\sqrt{2} \; P^{(B2)} |\sigma jm) = \sqrt{\tfrac{1}{2}} \; \{|\sigma j m) - (-1)^{j+m} |\sigma j, -m)\} \; \delta(m, n + n\sigma + 2np)$$

(7-25)

## B. CUBIC GROUPS

In the non-cubic groups, if the principal symmetry axis is chosen as the z-axis, the only possible values of the Eulerian angle $\beta$ for the operations of the group are 0 and $\pi$. These rotations transform a given $|\sigma j m)$ eigenfunction into either $|\sigma j m)$ or $|\sigma j, -m)$, multiplied by the appropriate phase factor (Eqs. 7-8 and 7-9). In the case of the cubic groups other values of $\beta$ are present. If the three fourfold axes of symmetry of a cube are selected as axes, the new possible value of $\beta$ is $\pi/2$. If one of the three-fold symmetry axes is chosen as z-axis, $\beta$ assumes the values $r$ and $\pi-r$, where $r$ is the tetrahedral angle. The $|\sigma j m)$

functions transform under these operations into linear combinations of $|\sigma j m'\rangle$ functions with the possible values of $\underline{m}'$ ranging, in general, from $-\underline{j}$ to $\underline{j}$.

The operators $P^{(\gamma)}_{\mu'\mu}$ transform the functions into linear combinations with $\mu'$ values of the form $\underline{m}' = \mu' + \underline{np}$, if the representations are chosen as previously indicated.

The symmetry functions may be obtained by the use of the projection operators. With our choice of representations it is relatively easy to obtain explicit expressions for them. We shall illustrate the procedure for the representations $A_1$, $F_1$, $E_{1/2}$ and $G_{3/2}$ of the group O. Our choice of representations is such that the $|\sigma j'm\rangle$ functions for $j' = 0, 1, 1/2, 3/2$, respectively, transform according to the representation matrices, so that

$$(\gamma\mu'|R|\gamma\mu) = (j'\mu'|R|j'\mu) = e^{i\mu'\alpha}\, d^{(j')}_{\mu'\mu}(\beta)\, e^{i\mu\gamma} \tag{7-26}$$

where $\mu$ and $\mu'$ assume the $2j'+1$ values from $\underline{j'}$ to $-\underline{j'}$.

The operation of the $P^{(\gamma)}_{\mu'\mu}$ on the functions $|\sigma j m\rangle$ is

$$P^{(\gamma)}_{\mu'\mu}|\sigma j m\rangle = \sum_{m'}|\sigma j m'\rangle(\sigma j m'|P^{(\gamma)}_{\mu'\mu}|\sigma j m\rangle$$

$$= \frac{d}{h}\sum_R R|\sigma j m\rangle(\gamma\mu'|R|\gamma\mu)^* \tag{7-27}$$

$$= \frac{d}{h}\sum_{m'}|\sigma j m'\rangle\sum_R(j m'|R|j m)(\gamma\mu'|R|\gamma\mu)^*$$

The coefficients of the various $|\sigma j m'\rangle$ may now be written, by use of Eqs. (5-9) and (7-26), in the form

$$(\sigma j m'|P^{(j')}_{\mu'\mu}|\sigma j m) = \sum_{\alpha,\beta,\gamma}\frac{d}{h}e^{i(m'-\mu')\alpha}\,e^{i(m-\mu)\gamma}\,d^{(j')}_{\mu'\mu}(\beta)\,d^{(j)}_{m'm}(\beta) \tag{7-28}$$

The summations over $\alpha$ and $\gamma$ for every value of $\beta$ may then be performed separately. With the sets of Eulerian angles given in Table 6-5 we obtain three types of terms.

For $\beta = 0$, $\alpha + \gamma = 0, \pi, \frac{\pi}{2}, -\frac{\pi}{2}$, and

$$d^{(j')}_{\mu'\mu}(0) = \delta(\mu',\mu) \qquad\qquad d^{(j)}_{m'm}(0) = \delta(m',m) \tag{7-29}$$

and the corresponding sum is

$$\delta(\mu',\mu)\,\delta(m',m)\sum_{a+\gamma}e^{i(m-\mu)(a+\gamma)} = 4\,\delta(\mu',\mu)\,\delta(m',m)\,\delta(m,\mu+4p) \qquad (7\text{-}30)$$

Similarly, for $\beta = \pi$, $a - \gamma = 0, \pi, \dfrac{\pi}{2}, -\dfrac{\pi}{2}$

$$d^{(j')}_{\mu'\mu}(\pi) = (-1)^{j'+\mu}\,\delta(\mu',-\mu) \qquad\qquad d^{(j)}_{m'm}(\pi) = (-1)^{j+m}\,\delta(m',-m) \qquad (7\text{-}31)$$

$$\delta(\mu',-\mu)\,\delta(m',-m)\sum_{a-\gamma}e^{-i(m-\mu)(a-\gamma)} = 4\,\delta(\mu',-\mu)\,\delta(m',-m)\,\delta(m,\mu+4p) \qquad (7\text{-}32)$$

For $\beta = \dfrac{\pi}{2}$, we have $a,\gamma = 0, \pi, \dfrac{\pi}{2}, -\dfrac{\pi}{2}$, but no simple expression for the $d^{j}_{m'm}$, so we will leave the sum in the form

$$d^{(j')}_{\mu'\mu}\left(\tfrac{\pi}{2}\right) d^{(j)}_{m'm}\left(\tfrac{\pi}{2}\right)\left(\sum_{a}e^{i(m'-\mu')a}\right)\left(\sum_{\gamma}e^{i(m-\mu)\gamma}\right) = 16\,d^{(j')}_{\mu'\mu}\left(\tfrac{\pi}{2}\right)d^{(j)}_{m'm}\left(\tfrac{\pi}{2}\right)\delta(m',\mu'+4p')\,\delta(m,\mu+4p) \quad (7\text{-}33)$$

In general, we may write the matrix elements of the projection operators as a sum of three terms

$$(\sigma j m'|P^{(\gamma)}_{\mu'\mu}|\sigma j m) = \delta(m',\mu'+4p')\,\delta(m,\mu+4p)$$

$$\times\; \frac{4d}{24}\left\{c(0)\,\delta(m',m) + c(\pi)(-1)^{j+m}\,\delta(m',-m) + c(\tfrac{\pi}{2})\,d^{(j)}_{m'm}(\tfrac{\pi}{2})\right\} \qquad (7\text{-}34)$$

For the representations considered, the coefficients $c(0)$, $c(\pi)$, and $c(\pi/2)$ are, as we have seen

$$c(0) = \delta(\mu',\mu)$$

$$c(\pi) = (-1)^{j'+\mu}\,\delta(\mu',-\mu) \qquad\qquad\qquad\qquad (7\text{-}35)$$

$$c(\tfrac{\pi}{2}) = 4d^{(j')}_{\mu'\mu}(\tfrac{\pi}{2})$$

TABLE 7-1

COEFFICIENTS IN THE EXPRESSION OF THE PROJECTION
OPERATORS. GROUP O. (CUBIC AXES)

| $\Gamma$ | $\mu'$ | $\mu$ | $c(0)$ | $c(\pi)$ | $c(\frac{\pi}{2})$ |
|---|---|---|---|---|---|
| $A_1$ | 0 | 0 | 1 | 1 | 4 |
| $A_2$ | 2 | 2 | 1 | 1 | -4 |
| $E$ { | 0 | 0 | 1 | 1 | -2 |
|  | 2 | 0 | 0 | 0 | $2\sqrt{3}$ |
| $E$ { | 0 | 2 | 0 | 0 | $2\sqrt{3}$ |
|  | 2 | 2 | 1 | 1 | 2 |
| $F_1$ { | 1 | 1 | 1 | 0 | 2 |
|  | 0 | 1 | 0 | 0 | $-2\sqrt{2}$ |
|  | -1 | 1 | 0 | 1 | 2 |
| $F_1$ { | 1 | 0 | 0 | 0 | $2\sqrt{2}$ |
|  | 0 | 0 | 1 | -1 | 0 |
|  | -1 | 0 | 0 | 0 | $-2\sqrt{2}$ |
| $F_1$ { | 1 | -1 | 0 | 1 | 2 |
|  | 0 | -1 | 0 | 0 | $-2\sqrt{2}$ |
|  | -1 | -1 | 1 | 0 | 2 |
| $F_2$ { | -1 | -1 | 1 | 0 | -2 |
|  | 2 | -1 | 0 | 0 | $2\sqrt{2}$ |
|  | 1 | -1 | 0 | 1 | -2 |
| $F_2$ { | -1 | 2 | 0 | 0 | $-2\sqrt{2}$ |
|  | 2 | 2 | 1 | -1 | 0 |
|  | 1 | 2 | 0 | 0 | $2\sqrt{2}$ |
| $F_2$ { | -1 | 1 | 0 | 1 | -2 |
|  | 2 | 1 | 0 | 0 | $2\sqrt{2}$ |
|  | 1 | 1 | 1 | 0 | -2 |

| $\Gamma$ | $\mu'$ | $\mu$ | $c(0)$ | $c(\pi)$ | $c(\pi/2)$ |
|---|---|---|---|---|---|
| $E_{1/2}$ { | 1/2 | 1/2 | 1 | 0 | $2\sqrt{2}$ |
|  | -1/2 | 1/2 | 0 | -1 | $-2\sqrt{2}$ |
| $E_{1/2}$ { | 1/2 | -1/2 | 0 | 1 | $2\sqrt{2}$ |
|  | -1/2 | -1/2 | 1 | 0 | $2\sqrt{2}$ |
| $E_{5/2}$ { | 5/2 | 5/2 | 1 | 0 | $-2\sqrt{2}$ |
|  | -5/2 | 5/2 | 0 | -1 | $2\sqrt{2}$ |
| $E_{5/2}$ { | 5/2 | -5/2 | 0 | 1 | $-2\sqrt{2}$ |
|  | -5/2 | -5/2 | 1 | 0 | $-2\sqrt{2}$ |
| $G_{3/2}$ { | 3/2 | 3/2 | 1 | 0 | $\sqrt{2}$ |
|  | 1/2 | 3/2 | 0 | 0 | $-\sqrt{6}$ |
|  | -1/2 | 3/2 | 0 | 0 | $\sqrt{6}$ |
|  | -3/2 | 3/2 | 0 | -1 | $-\sqrt{2}$ |
| $G_{3/2}$ { | 3/2 | 1/2 | 0 | 0 | $\sqrt{6}$ |
|  | 1/2 | 1/2 | 1 | 0 | $-\sqrt{2}$ |
|  | -1/2 | 1/2 | 0 | 1 | $-\sqrt{2}$ |
|  | -3/2 | 1/2 | 0 | 0 | $\sqrt{6}$ |
| $G_{3/2}$ { | 3/2 | -1/2 | 0 | 0 | $\sqrt{6}$ |
|  | 1/2 | -1/2 | 0 | -1 | $\sqrt{2}$ |
|  | -1/2 | -1/2 | 1 | 0 | $-\sqrt{2}$ |
|  | -3/2 | -1/2 | 0 | 0 | $-\sqrt{6}$ |
| $G_{3/2}$ { | 3/2 | -3/2 | 0 | 1 | $\sqrt{2}$ |
|  | 1/2 | -3/2 | 0 | 0 | $\sqrt{6}$ |
|  | -1/2 | -3/2 | 0 | 0 | $\sqrt{6}$ |
|  | -3/2 | -3/2 | 1 | 0 | $\sqrt{2}$ |

These coefficients may be obtained for the remaining representations in a similar form. Table 7-1 gives their values for all the operators for the group O.

The simplest linear combinations of $|jm)$ functions transforming according to the different irreducible representations are

$A_1 \quad |00)$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\mu = 0$

$A_2 \quad \{|32) - |3, -2)\}/\sqrt{2}$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\mu = 2$

$E \quad [|20), \{|22) + |2, -2)\}/\sqrt{2}]$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\mu = 0,2$

$F_1 \quad [|1\bar{1}), |10), |1, -1)]$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\mu = 1, 0, -1$

$F_2 \quad [|2, -1), \{|22) - |2, -2)\}/\sqrt{2}, -|2, 1)]$ $\qquad\qquad\qquad\qquad$ $\mu = -1, 2, 1$

$E_{\frac{1}{2}} \quad [|\tfrac{1}{2}\ \tfrac{1}{2}), |\tfrac{1}{2}, -\tfrac{1}{2})]$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\mu = \tfrac{1}{2}, -\tfrac{1}{2}$

$E_{\frac{5}{2}} \quad [\{|\tfrac{5}{2}\ \tfrac{5}{2}) - \sqrt{5}\,|\tfrac{5}{2}, -\tfrac{3}{2})\}/\sqrt{6}, \{-\sqrt{5}\,|\tfrac{5}{2}\ \tfrac{3}{2}) + |\tfrac{5}{2}, -\tfrac{5}{2})\}/\sqrt{6}]$ $\quad$ $\mu = \tfrac{5}{2}, -\tfrac{5}{2}$

$G_{\frac{3}{2}} \quad [|\tfrac{3}{2}\ \tfrac{3}{2}), |\tfrac{3}{2}\ \tfrac{1}{2}), |\tfrac{3}{2}, -\tfrac{1}{2}), |\tfrac{3}{2}, -\tfrac{3}{2})]$ $\qquad\qquad\qquad$ $\mu = \tfrac{3}{2}, \tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{3}{2}$

$$(7\text{-}36)$$

*Trigonal Axes*

In certain problems involving correlations between results for cubic symmetry and those obtained when some lower type of symmetry is present it is convenient to refer the $|jm)$ funtions to a system of axis other than the usual cubic axis. The symmetry functions referred to the cubic axes may be transformed by the methods of Section 5, but the linear combinations thus obtained are in general more complicated than the original ones. It is often preferable to set up the problem from the start in the desired set of axis and obtain cubic symmetry functions, which are the simplest in the new reference system, so that the correlation with the lower symmetry functions may also be facilitated.

The Eulerian angles for the operations of the cubic groups may be easily determined for the lower symmetry reference system, and the expressions for the projection operators and the symmetry functions are obtained as in the previous case.

A very frequent type of lower symmetry is that of trigonal symmetry. We may conveniently choose the trigonal set of axes along the following directions of the elementary cube

$$z' \equiv (1,1,1) \qquad x' \equiv (\tfrac{1}{2},-1,\tfrac{1}{2}) \qquad y' \equiv (1,0,-1)$$

The relative position of the cubic and trigonal sets of axes is illustrated in Fig. 7-1.



$$(\gamma, \beta, \alpha) = (\tfrac{\pi}{4}, \tfrac{\tau}{2}, -\tfrac{2\pi}{3})$$
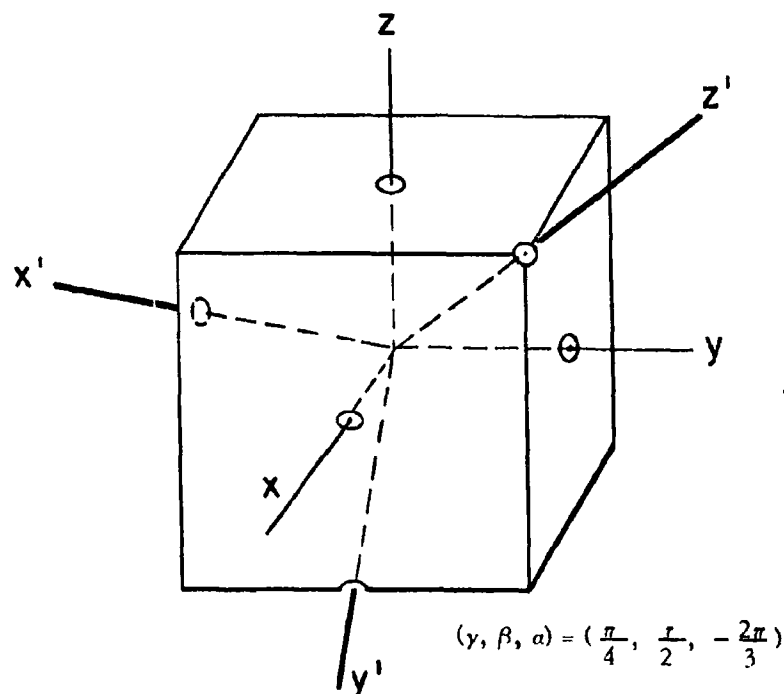
## TRIGONAL AXES
## FIG. 7 - 1

The Euierian angles corresponding to the operations of the octahedral group O referred to the trigonal axes system are given in Table 7-2. The operations are designated by the same symbols used for the cubic set of axes. The possible sets of angles may be summarized as follows

$$\beta = 0 \qquad \alpha+\gamma = 0, 2\pi/3, -2\pi/3$$

$$\beta = \pi \qquad \alpha-\gamma = 0, 2\pi/3, -2\pi/3$$

$$\beta = \tau, \tau-\pi \begin{cases} \alpha = 0, 2\pi/3, -2\pi/3 \\ \gamma-\pi = 0, 2\pi/3, -2\pi/3 \end{cases} \qquad (7\text{-}37)$$

# TABLE 7-2

## GROUP O: Eulerian Angles (Trigonal Axes)

| SUBGROUP T | | COSET T·C₂′ | |
|---|---|---|---|
| $R$ | $(\gamma, \beta, \alpha)$ | $R \cdot C_2'$ | $(\gamma, \beta, \alpha)$ |
| E | $(0,0,0)$ | $C_2'(-xz)$ | $(0, \pi, 0)$ |
| $C_2(z)$ | $(-\frac{\pi}{3}, r, -\frac{2\pi}{3})$ | $C_4(y)$ | $(-\frac{\pi}{3}, r-\pi, \frac{2\pi}{3})$ |
| $C_2(y)$ | $(\pi, r, 0)$ | $C_2'(xz)$ | $(\pi, r-\pi, 0)$ |
| $C_2(x)$ | $(\frac{\pi}{3}, r, \frac{2\pi}{3})$ | $C_4^{-1}(y)$ | $(\frac{\pi}{3}, r-\pi, -\frac{2\pi}{3})$ |
| $C_3(1,1,1)$ | $(\frac{2\pi}{3}, 0, 0)$ | $C_2'(-yz)$ | $(\frac{2\pi}{3}, \pi, 0)$ |
| $C_3(-1,1,-1)$ | $(\frac{\pi}{3}, r, -\frac{2\pi}{3})$ | $C_2'(yz)$ | $(\frac{\pi}{3}, r-\pi, \frac{2\pi}{3})$ |
| $C_3(1,-1,-1)$ | $(-\frac{\pi}{3}, r, 0)$ | $C_4^{-1}(x)$ | $(-\frac{\pi}{3}, r-\pi, 0)$ |
| $C_3(-1,-1,1)$ | $(\pi, r, \frac{2\pi}{3})$ | $C_4(x)$ | $(\pi, r-\pi, -\frac{2\pi}{3})$ |
| $C_3^{-1}(1,1,1)$ | $(-\frac{2\pi}{3}, 0, 0)$ | $C_2'(-xy)$ | $(-\frac{2\pi}{3}, \pi, 0)$ |
| $C_3^{-1}(-1,1,-1)$ | $(-\frac{\pi}{3}, r, \frac{2\pi}{3})$ | $C_2'(xy)$ | $(-\frac{\pi}{3}, r-\pi, -\frac{2\pi}{3})$ |
| $C_3^{1}(1,-1,-1)$ | $(\pi, r, -\frac{2\pi}{3})$ | $C_4^{-1}(z)$ | $(\pi, r-\pi, \frac{2\pi}{3})$ |
| $C_3^{-1}(-1,-1,1)$ | $(\frac{\pi}{3}, r, 0)$ | $C_4(z)$ | $(\frac{\pi}{3}, r-\pi, 0)$ |

The angle $r = 109°28'$ is the tetrahedral angle and

$$\cos r = -1/3, \qquad \sin r = 2\sqrt{2}/3 \qquad\qquad (7\text{-}38)$$

The operations of the subgroup T are those with $\beta = 0, r$, while for the coset $T \cdot C_2'$ we have $\beta = \pi, r + \pi$.

The irreducible representation matrices for $A_1$, $F_1$, $E_{1/2}$, and $G_{3/2}$ in terms of the Eulerian angles are the same as for the case of cubic set of axes, and they have been given in Table 6-4. Also, the matrices for $A_2$, $F_2$, and $E_{5/2}$ are chosen to be the same as for the corresponding conjugate representations $A_1$, $F_1$, and $E_{1/2}$ for the operations of the subgroup T, and the negatives for the operations of the coset $T \cdot C_2'$. However, the matrices for the irreducible representation E are now chosen as

$$\begin{bmatrix} \frac{1}{2}(3\cos\beta - 1)\, e^{i(\alpha+\gamma)} & 0 \\[2ex] 0 & \frac{1}{2}(3\cos\beta - 1)\, e^{-i(\alpha+\gamma)} \end{bmatrix} \qquad (7\text{-}39)$$

for the operations of the subgroup T, $(\beta = 0, r)$, and

$$\begin{bmatrix} 0 & -\frac{1}{2}(3\cos\beta + 1)\, e^{i(\alpha-\gamma)} \\[2ex] -\frac{1}{2}(3\cos\beta + 1)\, e^{-i(\alpha-\gamma)} & 0 \end{bmatrix} \qquad (7\text{-}40)$$

for the operations of the coset $T \cdot C_2'$, $(\beta = \pi, r - \pi)$.

The matrix elements of the projection operators may be written as a sum of four terms

$$(j\,m'|\, P^{(\gamma)}_{\mu'\mu} \,|\, j\,m) = \frac{3d}{24}\, \delta(m, \mu + 3p)\, \delta(m', \mu' + 3p')$$

$$\times \{\, c(0)\, \delta(m', m) + c(\pi)\, (-1)^{j+m}\, \delta(m', -m) \qquad\qquad (7\text{-}41)$$

$$+\, c^+(r)\, (-1)^{m-\mu}\, d^{(j)}_{m'm}(r) + c^-(r)\, (-1)^{j-\mu}\, d^{(j)}_{m',-m}(r) \,\}$$

The representations $A_1$, $E_{1/2}$, $F_1$, and $G_{3/2}$ have been chosen so that the $|\sigma\, j'\, m)$ functions for $j' = 0$, $1/2$, $1$, and $3/2$, respectively, transform according to the corresponding matrices, and the coefficients $c(0)$, $c(\pi)$, $c^+(r)$, and $c^-(r)$ are given by

$$c(0) = \delta(\mu', \mu)$$

$$c(\pi) = (-1)^{j'+\mu} \delta(\mu', -\mu)$$

$$c^+(r) = 3\, d^{(j')}_{\mu'\mu}(r)$$

$$c^-(r) = 3(-1)^{j'-\mu}\, d^{(j')}_{\mu',-\mu}(r)$$

$$(7\text{-}42)$$

For the representations $A_2$, $E_{5/2}$, and $F_2$, the coefficients $c(\pi)$ and $c^-(r)$ have opposite sign from those for $A_1$, $E_{1/2}$, and $F_1$, as previously indicated. The numerical values of the coefficients for all the representations are given in Table 7-3.

The simplest linear combinations of $|jm)$ functions transforming according to the matrices of the irreducible representations chosen are

| | | |
|---|---|---|
| $A_1$ | $\|00)$ | $\mu = 0$ |
| $A_2$ | $\{\sqrt{2}\|33) + \sqrt{5}\|30) - \sqrt{2}\|3,-3)\}/3$ | $\mu = 0$ |
| E | $[\{\sqrt{2}\|21) + \|2,-2)\}/\sqrt{3}, \{\|22) - \sqrt{2}\|2,-1)\}/\sqrt{3}]$ | $\mu = 1, -1$ |
| $F_1$ | $[\|11), \|10), \|1,-1)]$ | $\mu = 1, 0, -1$ |
| $F_2$ | $[\{-\|21) + \sqrt{2}\|2,-2)\}/\sqrt{3}, \|20), \{-\sqrt{2}\|22) - \|2,-1)\}/\sqrt{3}]$ | $\mu = 1, 0, -1$ |
| $E_{1/2}$ | $[\|\tfrac{1}{2}\tfrac{1}{2}), \|\tfrac{1}{2}, -\tfrac{1}{2})]$ | $\mu = \tfrac{1}{2}, -\tfrac{1}{2}$ |
| $E_{5/2}$ | $[\{\sqrt{5}\|\tfrac{5}{2}\tfrac{1}{2}) - 2\|\tfrac{5}{2}, -\tfrac{5}{2})\}/3, \{-2\|\tfrac{5}{2}\tfrac{5}{2}) - \sqrt{5}\|\tfrac{5}{2}, -\tfrac{1}{2})\}/3]$ | $\mu = \tfrac{1}{2}, -\tfrac{1}{2}$ |
| $G_{3/2}$ | $[\|\tfrac{3}{2}\tfrac{3}{2}), \|\tfrac{3}{2}\tfrac{1}{2}), \|\tfrac{3}{2}, -\tfrac{1}{2}), \|\tfrac{3}{2}, -\tfrac{3}{2})]$ | $\mu = \tfrac{3}{2}, \tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{3}{2}$ |

$$(7\text{-}43)$$

## GROUP T

As indicated previously, the matrices of the irreducible representations of the group O, with the exception of those for E and $G_{3/2}$, have been chosen so that they are also irreducible under the subgroup T. Accordingly, the symmetry functions obtained for the group O are also symmetry functions under T, with the correlation

# TABLE 7-3

## COEFFICIENTS IN THE EXPRESSION OF THE PROJECTION OPERATORS. GROUP O (Trigonal axes)

| $\Gamma'$ | $\mu'$ | $\mu$ | $c(0)$ | $c(\pi)$ | $c^+(r)$ | $c^-(r)$ |
|---|---|---|---|---|---|---|
| $A_1$ | 0 | 0 | 1 | 1 | 3 | 3 |
| $A_2$ | 0 | 0 | 1 | -1 | 3 | -3 |
| $E$ | 1 | 1 | 1 | 0 | -3 | 0 |
|  | -1 | 1 | 0 | 1 | 0 | -3 |
| $E$ | 1 | -1 | 0 | 1 | 0 | -3 |
|  | -1 | -1 | 1 | 0 | -3 | 0 |
| $F_1$ | 1 | 1 | 1 | 0 | 1 | 2 |
|  | 0 | 1 | 0 | 0 | -2 | 2 |
|  | -1 | 1 | 0 | 1 | 2 | 1 |
| $F_1$ | 1 | 0 | 0 | 0 | 2 | -2 |
|  | 0 | 0 | 1 | -1 | -1 | 1 |
|  | -1 | 0 | 0 | 0 | -2 | 2 |
| $F_1$ | 1 | -1 | 0 | 1 | 2 | 1 |
|  | 0 | -1 | 0 | 0 | 2 | -2 |
|  | -1 | -1 | 1 | 0 | 1 | 2 |
| $F_2$ | 1 | 1 | 1 | 0 | 1 | -2 |
|  | 0 | 1 | 0 | 0 | -2 | -2 |
|  | -1 | 1 | 0 | -1 | 2 | -1 |
| $F_2$ | 1 | 0 | 0 | 0 | 2 | 2 |
|  | 0 | 0 | 1 | 1 | -1 | -1 |
|  | -1 | 0 | 0 | 0 | -2 | -2 |
| $F_2$ | 1 | -1 | 0 | -1 | 2 | -1 |
|  | 0 | -1 | 0 | 0 | 2 | 2 |
|  | -1 | -1 | 1 | 0 | 1 | -2 |

| $\Gamma$ | $\mu'$ | $\mu$ | $c(0)$ | $c(\pi)$ | $c^+(r)$ | $c^-(r)$ |
|---|---|---|---|---|---|---|
| $E_{1/2}$ | 1/2 | 1/2 | 1 | 0 | $\sqrt{3}$ | $\sqrt{6}$ |
|  | -1/2 | 1/2 | 0 | -1 | $-\sqrt{6}$ | $\sqrt{3}$ |
| $E_{1/2}$ | 1/2 | -1/2 | 0 | 1 | $\sqrt{6}$ | $-\sqrt{3}$ |
|  | -1/2 | -1/2 | 1 | 0 | $\sqrt{3}$ | $\sqrt{6}$ |
| $E_{5/2}$ | 1/2 | 1/2 | 1 | 0 | $\sqrt{3}$ | $-\sqrt{6}$ |
|  | -1/2 | 1/2 | 0 | 1 | $-\sqrt{6}$ | $-\sqrt{3}$ |
| $E_{5/2}$ | 1/2 | -1/2 | 0 | -1 | $\sqrt{6}$ | $\sqrt{3}$ |
|  | -1/2 | -1/2 | +1 | 0 | $\sqrt{3}$ | $-\sqrt{6}$ |
| $G_{3/2}$ | 3/2 | 3/2 | 1 | 0 | $\sqrt{1/3}$ | $\sqrt{8/3}$ |
|  | 1/2 | 3/2 | 0 | 0 | $-\sqrt{2}$ | 2 |
|  | -1/2 | 3/2 | 0 | 0 | 2 | $\sqrt{2}$ |
|  | -3/2 | 3/2 | 0 | -1 | $-\sqrt{8/3}$ | $\sqrt{1/3}$ |
| $G_{3/2}$ | 3/2 | 1/2 | 0 | 0 | $\sqrt{2}$ | -2 |
|  | 1/2 | 1/2 | 1 | 0 | $-\sqrt{3}$ | 0 |
|  | -1/2 | 1/2 | 0 | 1 | 0 | $\sqrt{3}$ |
|  | -3/2 | 1/2 | 0 | 0 | 2 | $\sqrt{2}$ |
| $G_{3/2}$ | 3/2 | -1/2 | 0 | 0 | 2 | $\sqrt{2}$ |
|  | 1/2 | -1/2 | 0 | -1 | 0 | $-\sqrt{3}$ |
|  | -1/2 | -1/2 | 1 | 0 | $-\sqrt{3}$ | 0 |
|  | -3/2 | -1/2 | 0 | 0 | $-\sqrt{2}$ | 2 |
| $G_{3/2}$ | 3/2 | -3/2 | 0 | 1 | $\sqrt{8/3}$ | $-\sqrt{1/3}$ |
|  | 1/2 | -3/2 | 0 | 0 | 2 | $\sqrt{2}$ |
|  | -1/2 | -3/2 | 0 | 0 | $\sqrt{2}$ | -2 |
|  | -3/2 | -3/2 | 1 | 0 | $\sqrt{1/3}$ | $\sqrt{8/3}$ |

$$\begin{array}{ccc}
\underline{\text{Group O}} & & \underline{\text{Group T}} \\
A_1, A_2 & \longrightarrow & A \\
F_1, F_2 & \longrightarrow & F \\
E_{1/2}, E_{5/2} & \longrightarrow & E_{1/2}
\end{array}$$

The self-conjugate representations E and $G_{3/2}$ of the group O are reducible under T. The reduction of the corresponding matrices chosen for the group O may be accomplished by a unitary transformation

$$\Gamma_T = A^{-1} \Gamma_O A \tag{7-44}$$

where the matrix $A$ is given by Eq. (6-17) or (6-18) for the representations E or $G_{3/2}$, respectively.

The corresponding symmetry functions are obtained from those for the group O by the transformation

$$\tilde{\Psi}_T = \tilde{\Psi}_O A \tag{7-45}$$

The simplest linear combinations of $|jm\rangle$ eigenfunctions obtained for these representations are

$$E_a = \frac{1}{2} [\sqrt{2} |20\rangle + i |22\rangle + i |2, -2\rangle]$$

$$E_b = \frac{1}{2} [\sqrt{2} |20\rangle - i |22\rangle - i |2, -2\rangle] \tag{7-46}$$

$$G_a \begin{cases} \dfrac{1}{\sqrt{2}} [|\tfrac{3}{2}, \tfrac{3}{2}\rangle + i |\tfrac{3}{2}, -\tfrac{1}{2}\rangle] \\[2mm] -\dfrac{1}{\sqrt{2}} [i |\tfrac{3}{2}, \tfrac{1}{2}\rangle + |\tfrac{3}{2}, -\tfrac{3}{2}\rangle] \end{cases} \tag{7-47}$$

$$G_b \begin{cases} \dfrac{1}{\sqrt{2}} [-i|\tfrac{3}{2}, \tfrac{1}{2}\rangle + |\tfrac{3}{2}, -\tfrac{3}{2}\rangle] \\[2mm] \dfrac{1}{\sqrt{2}} [|\tfrac{3}{2}, \tfrac{3}{2}\rangle - i |\tfrac{3}{2}, -\tfrac{1}{2}\rangle] \end{cases}$$

*GROUP* **T**$_d$

The symmetry functions for the irreducible representations of the group $T_d$ may be deduced from those of the group O by simple considerations.

If the $|jm\rangle$ eigenfunctions have even parity, they transform under the operations of $T_d$ in the same way as under the operations of O. Since we have chosen the same matrix representations for both groups, we also obtain the same linear combinations of $|jm\rangle$ eigenfunctions.

If the $|jm\rangle$ eigenfunctions have odd parity it is sufficient to notice that they transform under the operations of $T_d$ in the same form as the products $|A_2\rangle |jm\rangle$ transform under the corresponding operations of the group O. Consequently, the coefficients of the $|jm\rangle$ eigenfunctions of odd parity in the symmetry functions which belong to a given irreducible representation of $T_d$ are the same as for the corresponding $|jm\rangle$ functions which belong to the conjugate representation of the group O. For the self-conjugate representations, E and $G_{3/2}$, the preceding argument requires that the partner functions be taken in different order and with different phases from those for the group O or even parity functions. If the symmetry functions are designated by the index $\mu$ that labels the row of the irreducible representation of O to which the function $|\mu\rangle$ belongs, the partners have to be chosen according to the following scheme

| O Group<br>$T_d$, even parity | | $T_d$, odd parity |
|---|---|---|
| E | $\|0\rangle$, $\|2\rangle$ | $\|2\rangle$, $-\|0\rangle$ |
| $G_{3/2}$ | $\|3/2\rangle$, $\|1/2\rangle$, $\|-1/2\rangle$, $\|-3/2\rangle$ | $-\|-1/2\rangle$, $\|-3/2\rangle$, $\|3/2\rangle$, $-\|1/2\rangle$ |

This result will appear evident later on, when the coupling coefficients for the point groups are considered.

In different words, it may be said that the E or $G_{3/2}$ symmetry functions $|\mu_1\rangle$, $|\mu_2\rangle$, ...., if their parity is odd, form basis for a representation of $T_d$ which is equivalent to the one they afford for the group O, but not identical. In order to obtain a set which transforms according to the latter, they have to be subjected to an appropriate unitary transformation, which for our choice of representations leads to the result quoted.

## GROUPS $T_h$ AND $O_h$

These are direct product groups $I \times T$ and $O \times T$. Functions that belong to a given irreducible representation of T (or O) belong to the corresponding g or u representations of $T_h$ (or $O_h$), depending on whether they have even or odd parity, respectively.

# 8. COUPLING COEFFICIENTS

## A. SPHERICAL BASIS

Let us consider two angular momentum operators, $J_1$ and $J_2$, with eigenfunctions $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$. The subscripts 1 and 2 refer to two independent spaces (two particles or systems, orbital and spin coordinates of a particle or system, etc.) and therefore every component of one operator commutes with every component of the other.

The sum

$$J_1 + J_2 = J \tag{8-1}$$

is also an angular momentum operator and its components

$$J_{1\alpha} + J_{2\alpha} = J_\alpha \qquad (\alpha = x, y, \text{ or } z) \tag{8-2}$$

satisfy the usual commutation rules.

$$J \times J = iJ \tag{8-3}$$

It is possible therefore to find eigenfunctions $|jm\rangle$ satisfying the eigenvalue equations

$$J^2 |jm\rangle = |jm\rangle\, j(j + 1)$$
$$J_z |jm\rangle = |jm\rangle\, m \tag{8-4}$$

The $(2j_1 + 1)(2j_2 + 1)$ functions of the type

$$|j_1 m_1\rangle\, |j_2 m_2\rangle = |j_1 m_1 j_2 m_2\rangle \tag{8-5}$$

form the basis of the direct product representation (or uncoupled representation). They are eigenfunctions of the z-component of the total angular momentum, with eigenvalues $m = m_1 + m_2$

$$(J_{1z} + J_{2z})|j_1 m_1\rangle|j_2 m_2\rangle = |j_1 m_1\rangle|j_2 m_2\rangle\,(m_1 + m_2) \tag{8-6}$$

but are not, in general, eigenfunctions of the total $J^2$. The product functions may be classified according to the values of $m = m_1 + m_2$. There is one function, $|j_1 j_1\rangle|j_2 j_2\rangle$,

for $m = j_1 + j_2$; two functions, $|j_1 j_1\rangle|j_2 j_2 - 1)$ and $|j_1 j_1 - 1)|j_2 j_2)$ for $m = j_1 + j_2 - 1;\ldots,$ $2j_2 + 1$ or $2j_1 + 1$ for $m = |j_1 - j_2|;\ldots,$ and finally one for $m = -(j_1 + j_2)$. By simple considerations which we shall not go into, it may be proved that the possible eigenvalues $j$ of Eq. (8-4) are

$$ j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2| $$

The eigenfunctions $|jm)$ are linear combinations of the above product functions with $m_1 + m_2 = m$

$$ |jm) = \sum_{m_1} |j_1 m_1) |j_2 m_2) (j_1 m_1 j_2 m_2 | jm) \tag{8-7} $$

The summation runs only over the possible values of one of the indices $m_1$ or $m_2$, since their sum is fixed.

The coefficients $(j_1 m_1 j_2 m_2 | jm)$ are the so-called vector-coupling, Clebsch-Gordan, or Wigner's coefficients. Since the basis functions in both coupled and uncoupled schemes are assumed orthonormal, the matrices of these coefficients for a given $\underline{m}$ are unitary. Moreover, the phase-factors are usually chosen so that the transformation coefficients are real, and the matrices are orthogonal. The orthogonality relations are

$$ \sum_{m_1} (j_1 m_1 j_2 m_2 | jm) (j_1 m_1 j_2 m_2 | j'm) = \delta(j, j') $$

$$ \sum_{j} (j_1 m_1 j_2 m_2 | jm) (j_1 m_1' j_2 m_2' | jm) = \delta(m_1, m_1') \tag{8-8} $$

where it is understood that $m_1' + m_2' = m$.

*Recursion Relations*

There is an important recursion formula which connects three coupling coefficients with the same $j_1, j_2,$ and $j_3$, and adjacent values of the $m$'s. It may be obtained by applying the m-lowering operator

$$ J_- = (J_{3x} - i J_{3y}) = (J_{1x} + J_{2x}) - i (J_{1y} + J_{2y}) \tag{8-9} $$

to both sides of Eq. (8-7) followed by premultiplication by $(j_1 m_1 | (j_2 m_2 |$. After relabeling $m_3$ the result may be written as

$$\{(j_3 - m_3)(j_3 + m_3 + 1)\}^{1/2} <j_1 m_1 j_2 m_2 | j_3 m_3> =$$

$$\text{(8-10)}$$

$$\{(j_1 - m_1)(j_1 + m_1 + 1)\}^{1/2}(j_1 m_1 + 1 \ j_2 m_2 | j_3 m_3 + 1) + \{(j_2 - m_2)(j_2 + m_2 + 1)\}^{1/2}(j_1 m_1 j_2 m_2 + 1 | j_3 m_3 + 1)$$

A similar expression may be obtained by use of the m-raising operator $J_+$

$$\{(j_3 + m_3)(j_3 - m_3 + 1)\}^{1/2}(j_1 m_1 j_2 m_2 | j_3 m_3) =$$

$$\text{(8-11)}$$

$$\{(j_1 + m_1)(j_1 - m_1 + 1)\}^{1/2}(j_1 m_1 - 1 \ j_2 m_2 | j_3 m_3 - 1) + \{(j_2 + m_2)(j_2 - m_2 + 1)\}^{1/2}(j_1 m_1 j_2 m_2 - 1 | j_3 m_3 - 1)$$

If the coupling coefficients for given $j_1$, $j_2$, $j_3$ are written as the elements of a matrix with columns labelled by the values of $m_1$, and the rows by those of $m_2$, the recursion relations connect those elements whose relative positions are indicated below

|          | $\ldots$ | $m_1 + 1$ | $m_1$ | $\ldots$ |
|----------|----------|-----------|-------|----------|
| $\ldots$ |          |           |       |          |
| $m_2 + 1$ |          |           | $(m_1, m_2 + 1)$ |  |
| $m_2$    |          | $(m_1 + 1, m_2)$ | $(m_1, m_2)$ |  |
| $\ldots$ |          |           |       |          |

|          | $\ldots$ | $m_1$ | $m_1 - 1$ | $\ldots$ |
|----------|----------|-------|-----------|----------|
| $\ldots$ |          |       |           |          |
| $m_2$    |          | $(m_1, m_2)$ | $(m_1 - 1, m_2)$ |  |
| $m_2 - 1$ |          | $(m_1, m_2 - 1)$ |  |  |
| $\ldots$ |          |       |           |          |

The recursion formulae together with the orthonormality conditions suffice to determine all the coupling coefficients for given $j_1, j_2, j_3$, except from a common arbitrary phase factor.

Thus, for example for $m_1 = j_1$ Eq. (8-10) becomes a one-term recursion formula, so that the ratios of the coupling coefficients for $m_1 = j_1$ to one of them may be determined. This particular element may be obtained by the normalization condition. The phase factor is chosen to be +1, and all these elements will be positive. Similarly, for $m_2 = -j_2$, Eq. (8-11) also becomes a one-term recursion formula and all the elements in the last row of the matrices in the previous scheme may be obtained. Also, they are all positive. The rest of the elements may then be obtained from those of the first column and the last row by using either of the recursion relations.

*General Expression*

The general expression for the coupling coefficients given by Wigner[1] is the following:

$$(j_1 m_1 j_2 m_2 | j_3 m_3) = \delta(m_1 + m_2, m_3)(2j_3 + 1)^{1/2}$$

$$\times \left\{ \frac{(-j_1 + j_2 + j_3)!(j_1 - j_2 + j_3)!(j_1 + j_2 - j_3)!(j_3 + m_3)!(j_3 - m_3)!}{(j_1 + j_2 + j_3 + 1)!(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!} \right\}^{1/2} \qquad (8\text{-}12)$$

$$\times \sum_\nu \frac{(-1)^{j_2 + m_2 + \nu}(j_1 - m_1 + \nu)!(j_2 + j_3 + m_1 - \nu)!}{\nu!(-j_1 + j_2 + j_3 - \nu)!(j_3 + m_3 - \nu)!(-j_2 + j_1 - m_3 + \nu)!}$$

The summation index $\nu$ assumes all integral values that make the arguments of the factorials non-negative.

The formula is simpler for some particular values of the m's. A few particular cases are of interest, and we shall express them in terms of binomial coefficients.

For $m_1 = m_2 = m_3 = 0$, if $j_1 + j_2 + j_3 =$ odd,

$$(j_1 0 j_2 0 | j_3 0) = 0 \qquad (8\text{-}13)$$

if $j_1 + j_2 + j_3 = 2g$ = even,

$$(j_1 0 j_2 0 | j_3 0) = (-1)^{g - j_3} \left\{ \frac{2j_3 + 1}{j_1 + j_2 + j_3 + 1} \right\}^{1/2} \frac{\begin{pmatrix} g \\ j_1 \end{pmatrix} \begin{pmatrix} j_1 \\ g - j_3 \end{pmatrix}}{\left\{ \begin{pmatrix} 2g \\ 2j_1 \end{pmatrix} \begin{pmatrix} 2j_1 \\ 2g - 2j_3 \end{pmatrix} \right\}^{1/2}} \quad (8\text{-}14)$$

It should be noticed that the last factor is symmetric in $j_1, j_2, j_3$. In actual calculations it is advantageous to denote the smallest $j_i$ by $j_1$ and the largest by $j_3$ in Eq. (8-14).

For $m_1 = j_1$,

$$(j_1 j_1 j_2 m_2 | j_3 m_3) = \left\{ \frac{2j_3 + 1}{j_1 + j_2 + j_3 + 1} \right\}^{1/2} \left\{ \frac{\begin{pmatrix} 2j_1 \\ j_1 - j_2 + j_3 \end{pmatrix} \begin{pmatrix} -j_1 + j_2 + j_3 \\ j_3 - m_3 \end{pmatrix}}{\begin{pmatrix} j_1 + j_2 + j_3 \\ j_3 + m_3 \end{pmatrix}} \right\}^{1/2} \quad (8\text{-}15)$$

For $m_2 = -j_2$,

$$(j_1 m_1 j_2, -j_2 | j_3 m_3) = \left\{ \frac{2j_3 + 1}{j_1 + j_2 + j_3 + 1} \right\}^{1/2} \left\{ \frac{\begin{pmatrix} 2j_2 \\ -j_1 + j_2 + j_3 \end{pmatrix} \begin{pmatrix} j_1 - j_2 + j_3 \\ j_1 - m_1 \end{pmatrix}}{\begin{pmatrix} j_1 + j_2 + j_3 \\ j_1 + m_1 \end{pmatrix}} \right\}^{1/2} \quad (8\text{-}16)$$

·For $m_3 = j_3$

$$(j_1 m_1 j_2 m_2 | j_3 j_3) = (-1)^{j_1 - m_1} \left\{ \frac{2j_3 + 1}{j_1 + j_2 + j_3 + 1} \right\}^{1/2} \left\{ \frac{\begin{pmatrix} 2j_3 \\ j_1 - j_2 + j_3 \end{pmatrix} \begin{pmatrix} j_1 + j_2 - j_3 \\ j_1 - m_1 \end{pmatrix}}{\begin{pmatrix} j_1 + j_2 + j_3 \\ j_1 + m_1 \end{pmatrix}} \right\}^{1/2} \quad (8\text{-}17)$$

Also, for $j_3 = j_1 + j_2, (m_3 \geqslant 0)$

$$(j_1 m_1 j_2 m_2 | j_1 + j_2 m_3) = \left\{ \frac{\begin{pmatrix} j_3 - m_3 \\ j_1 - m_1 \end{pmatrix} \begin{pmatrix} j_3 + m_3 \\ j_3 - m_3 \end{pmatrix}}{\begin{pmatrix} (j_1 + j_2 + j_3 + 1) \end{pmatrix} \begin{pmatrix} 2j_3 \\ 2j_1 \end{pmatrix}} \right\}^{1/2} \quad (8\text{-}18)$$

*The 3-j Symbols*

There are several different notations in use for the vector-coupling coefficients. A summary is given by Edmonds.[2] In addition, "symmetrized" coefficients have been introduced. The most widely accepted are the 3-j symbols introduced by Wigner. These are defined as

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{(2j_3 + 1)^{1/2}} \; (j_1 m_1 j_2 m_2 | j_3, -m_3) \tag{8-19}$$

with $m_1 + m_2 + m_3 = 0$.

The most obvious advantage is that the existing symmetry relations take the simplest form in terms of the 3-j symbols.

The symmetry relations between 3-j symbols with the same values of $j_1, j_2$, and $j_3$ may be stated as follows:

An even permutation of the columns leaves their value unchanged, an odd permutation introduces the factor $(-1)^{j_1 + j_2 + j_3}$.

A change in sign of all the $m_i$'s introduces the factor $(-1)^{j_1 + j_2 + j_3}$.

They may be expressed as follows:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 + j_2 + j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix}$$

and $\hspace{11cm}$ (8-20)

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 + j_2 + j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

If the parameters are all different, these relations connect twelve coefficients.

The orthogonality relations (Eq. 8-8) are slightly modified if expressed in terms of 3-j coefficients

$$\sum_{m_1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{\delta(j_3, j_3')}{(2j_3+1)}$$

(8-21)

$$\sum_{j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} (2j_3+1) = \delta(m_1, m_1')$$

where $m_1 + m_2 + m_3 = m_1' + m_2' + m_3 = 0$

### Calculation of 3-j Coefficients

The expression for the 3-j coefficients may be written in the following form

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \delta(m_1 + m_2 + m_3, 0) \left\{ \frac{(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)!}{(-j_1+j_2+j_3)!(j_1-j_2+j_3)!(j_1+j_2-j_3)!(j_1+j_2+j_3+1)!} \right\}^{1/2}$$

(8-22)

$$\times \sum_{\nu} (-1)^{\nu+j_1-j_2-m_3} \begin{pmatrix} j_1+j_2-j_3 \\ \nu \end{pmatrix} \begin{pmatrix} j_1-j_2+j_3 \\ j_1-m_1-\nu \end{pmatrix} \begin{pmatrix} -j_1+j_2+j_3 \\ j_2+m_2-\nu \end{pmatrix}$$

The sum is taken over all integral values of $\nu$ which make the arguments of the factorials non-negative. The same is true for the possible values of $j_1, j_2, j_3$, which should satisfy the triangular condition.

The factor in front of the summation is symmetric in the subindices 1, 2, and 3, so that the summations themselves have the same symmetry properties as the 3-j coefficients. Also they are sums of products of binomial coefficients and therefore integral numbers, and satisfy recursion relations much simpler than those for the coupling coefficients. These are very useful for numerical calculations of the coupling coefficients.

The summations may be denoted by $\Sigma \begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{vmatrix}$. The recursion relations that correspond to Eqs. (8-10) and (8-11) are

8-7

$$(j_3+m_3)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{vmatrix} + (j_1+m_1+1)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1+1 & m_2 & m_3-1 \end{vmatrix} + (j_2+m_2+1)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2+1 & m_3-1 \end{vmatrix} = 0 \qquad (8\text{-}23)$$

$$(j_3-m_3)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{vmatrix} + (j_1-m_1+1)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1-1 & m_2 & m_3+1 \end{vmatrix} + (j_2-m_2+1)\,\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2-1 & m_3+1 \end{vmatrix} = 0 \qquad (8\text{-}24)$$

Another very useful recursion formula relates the sigmas with those for adjacent values of the j's and takes the simple form

$$\Sigma\begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{vmatrix} = \Sigma\begin{vmatrix} j_1-1/2 & j_2-1/2 & j_3 \\ m_1-1/2 & m_2+1/2 & m_3 \end{vmatrix} - \Sigma\begin{vmatrix} j_1-1/2 & j_2-1/2 & j_3 \\ m_1+1/2 & m_2-1/2 & m_3 \end{vmatrix} \qquad (8\text{-}25)$$

Thus, for example, the $\Sigma$-matrices for

$$j_1 = 1, j_2 = 2, j_3 = 3 \text{ and } j_1 = 3/2, j_2 = 5/2, j_3 = 3$$

are



| $m_2$ \ $m_1$ | 1 | 0 | -1 |
|---|---|---|---|
| 2 | 1 | -2 | 1 |
| 1 | -4 | 8 | -4 |
| 0 | 6 | -12 | 6 |
| -1 | -4 | 8 | -4 |
| -2 | 1 | -2 | 1 |

| $m_2$ \ $m_1$ | 3/2 | 1/2 | -1/2 | -3/2 |
|---|---|---|---|---|
| 5/2 | 0 | -1 | 2 | -1 |
| 3/2 | 1 | 2 | -7 | 4 |
| 1/2 | -4 | 2 | 8 | -6 |
| -1/2 | 6 | -8 | -2 | 4 |
| -3/2 | -4 | 7 | -2 | -1 |
| -5/2 | 1 | -2 | 1 | 0 |

The second may be calculated from the first by simply taking the difference between two elements, whose relative positions are indicated in the scheme.

The expressions for the sigmas for the particular values $m_1 = j_1$ and $m_2 = -j_2$ are of interest since all the others in a given matrix may be obtained from them by means of the recursion relations (8-23,24).

For $m_1 = j_1$

$$\Sigma \begin{bmatrix} j_1 & j_2 & j_3 \\ j_1 & m_2 & m_3 \end{bmatrix} = (-1)^{j_1-j_2-m_3} \begin{pmatrix} -j_1 + j_2 + j_3 \\ j_2 + m_2 \end{pmatrix} \tag{8-26}$$

and for $m_2 = -j_2$

$$\Sigma \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & -j_2 & m_3 \end{bmatrix} = (-1)^{j_1-j_2-m_3} \begin{pmatrix} j_1 - j_2 + j_3 \\ j_1 - m_1 \end{pmatrix} \tag{8-27}$$

*Coupling Rules for the Rotation Matrices*

The expression for the coupling of angular momentum eigenfunctions thus far considered is

$$|j_3 m_3\rangle = \sum_{m_1} |j_1 m_1\rangle |j_2 m_2\rangle (j_1 m_1 j_2 m_2 | j_3 m_3) \tag{8-28}$$

where $m_3 = m_1 + m_2$ and the $j_i$'s satisfy the triangular condition $j_1 + j_2 \geq j_3 \geq |j_1 - j_2|$. The inverse relation is

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_{j_3} |j_3 m_3\rangle (j_1 m_1 j_2 m_2 | j_3 m_3) \tag{8-29}$$

The coefficients may be written as either $(j_1 m_1 j_2 m_2 | j_3 m_3)$ or $(j_3 m_3 | j_1 m_1 j_2 m_2)$ in virtue of the orthogonal character of the transformation.

It should be remembered at this point that $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are functions in two independent spaces while $|j_3 m_3\rangle$ is a function in the product space. Thus, for example, if

$$|j_1 m_1\rangle = Y_{j_1}^{m_1} (\theta_1, \phi_1)$$

$$|j_2 m_2\rangle = Y_{j_2}^{m_2} (\theta_2, \phi_2)$$

then $|j_3 m_3\rangle$ is a function of $\theta_1$, $\phi_1$, $\theta_2$, and $\phi_2$, but not a spherical harmonic, although it transforms under rotations in the same way.

The coupling expressions for spherical harmonics with the same argument may be obtained from those for the matrix elements of the rotation matrices. If the rotation operator $R(\alpha\beta\gamma)$ is applied to both sides of Eq. (8-28), we obtain according to Eq. (5-9)

$$\cdot \sum_{m_3'} |j_3 m_3'\rangle \, D_{m_3' m_3}^{(j_3)}(\alpha\beta\gamma)$$

$$= \sum_{m_1 m_1' m_2'} |j_1 m_1'\rangle \, |j_2 m_2'\rangle \, D_{m_1' m_1}^{(j_1)}(\alpha\beta\gamma) \, D_{m_2' m_2}^{(j_2)}(\alpha\beta\gamma) \, (j_1 m_1 j_2 m_2 | j_3 m_3)$$

(8-30)

If we premultiply scalarly by a particular $(j_3 m_3'|$ only one term on the left hand side remains, while on the right hand side the only non-vanishing terms are those for which $m_1' + m_2' = m_3'$, and we obtain

$$D_{m_3' m_3}^{(j_3)}(\alpha\beta\gamma) = \sum_{m_1 m_1'} (j_1 m_1' j_2 m_2' | j_3 m_3')(j_1 m_1 j_2 m_2 | j_3 m_3) \, D_{m_1' m_1}^{(j_1)}(\alpha\beta\gamma) \, D_{m_2' m_2}^{(j_2)}(\alpha\beta\gamma)$$

(8-31)

Similarly, from Eq. (8-29) the inverse relation may be derived

$$D_{m_1' m_1}^{(j_1)}(\alpha\beta\gamma) \, D_{m_2' m_2}^{(j_2)}(\alpha\beta\gamma) = \sum_{j_3} (j_1 m_1' j_2 m_2' | j_3 m_3')(j_1 m_1 j_2 m_2 | j_3 m_3) D_{m_3' m_3}^{(j_3)}(\alpha\beta\gamma)$$

(8-32)

where, as indicated, $m_3 = m_1 + m_2$ and $m_3' = m_1' + m_2'$.

It is more convenient to use in place of Eq. (8-31) another expression involving only one summation. This may be obtained from Eq (8-30) on premultiplication by a particular product function $(j_1 m_1'| \, (j_2 m_2'|$ and taking into account the orthonormal properties of these basis functions. One obtains

$$(j_1 m_1' j_2 m_2' | j_3 m_3') D_{m_3' m_3}^{(j_3)}(\alpha\beta\gamma) = \sum_{m_1} (j_1 m_1 j_2 m_2 | j_3 m_3) D_{m_1' m_1}^{(j_1)}(\alpha\beta\gamma) \, D_{m_2' m_2}^{(j_2)}(\alpha\beta\gamma)$$

(8-33)

The coupling rules for spherical harmonics with the same argument may now be obtained by setting $m_1' = m_2' = m_3' = 0$ in Eqs. (8-32) and (8-33), and making use of the relation between the $D_{0m}^{(\ell)}(\alpha\beta\phi)$ and the $Y_\ell^m(\theta,\phi)$ given by Eq. (5-30). The results are

$$Y_{\ell_3}^{m_3}(\theta,\phi) = \frac{1}{(\ell_1 0\, \ell_2 0\,|\,\ell_3 0)}\left[\frac{4\pi(2\ell_3+1)}{(2\ell_1+1)(2\ell_2+1)}\right]^{\frac{1}{2}} \sum_{m_1} (\ell_1 m_1 \ell_2 m_2\,|\,\ell_3 m_3)\, Y_{\ell_1}^{m_1}(\theta,\phi)\, Y_{\ell_2}^{m_2}(\theta,\phi)$$

(8-34)

and

$$Y_{\ell_1}^{m_1}(\theta,\phi)Y_{\ell_2}^{m_2}(\theta,\phi) = \sum_{\ell_3}\left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right]^{\frac{1}{2}} (\ell_1 0\, \ell_2 0\,|\,\ell_3 0)(\ell_1 m_1 \ell_2 m_2\,|\,\ell_3 m_3)\, Y_{\ell_3}^{m_3}(\theta,\phi)$$

(8-35)

*Matrix Elements of Spherical Harmonics*

From these coupling relations one may now deduce the expressions for the integral of the product of three rotation matrices or three spherical harmonics. If Eq. (8-32) is premultiplied by a particular $D_{m_3'm_3}^{(j_3)*}$ and integrated over the range of the three Eulerian angles we obtain, by considering the orthogonality properties

$$\int D_{m_3'm_3}^{(j_3)*}\, D_{m_2'm_2}^{(j_2)}\, D_{m_1'm_1}^{(j_1)}\; dR$$

(8-36)

$$= \left(D_{m_3'm_3}^{(j_3')}\,|\,D_{m_2'm_2}^{(j_2)}\,|\,D_{m_1'm_1}^{(j_1)}\right) = \frac{8\pi^2}{(2j_3+1)}\, (j_1 m_1' j_2 m_2'\,|\,j_3 m_3')(j_1 m_1 j_2 m_2\,|\,j_3 m_3)$$

Similarly, the integral of the product of three spherical harmonics is

$$\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\;\; Y_{\ell_3}^{m_3}(\theta,\phi)^*\; Y_{\ell_2}^{m_2}(\theta,\phi)\; Y_{\ell_1}^{m_1}(\theta,\phi)$$

(8-37)

$$= \left(Y_{\ell_3}^{m_3}\,|\,Y_{\ell_2}^{m_2}\,|\,Y_{\ell_1}^{m_1}\right) = \left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right]^{\frac{1}{2}} (\ell_1 0\, \ell_2 0\,|\,\ell_3 0)(\ell_1 m_1 \ell_2 m_2\,|\,\ell_3 m_3)$$

This may be written in terms of the 3-j symbols,

$$(Y_{\ell_3}^{m_3}\,|\,Y_{\ell_2}^{m_2}\,|\,Y_{\ell_1}^{m_1}) = (-1)^{m_3}\left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi}\right]^{\frac{1}{2}}\begin{pmatrix}\ell_1 \ell_2 \ell_3\\0\;0\;0\end{pmatrix}\begin{pmatrix}\ell_1 & \ell_2 & \ell_3\\m_1 & m_2 & -m_3\end{pmatrix}$$ (8-38)

This expression is very important for the determination of the matrix elements of many operators of interest in physical problems. For example, the crystal field potential acting on one electron may be expanded as a series of spherical harmonics. The matrix elements of the potential between electronic states with definite angular momentum may be expressed in terms of the 3-j coefficients. The matrix elements for other sets of basis functions, such as the symmetry functions corresponding to the actual symmetry point group of the crystal, may then be obtained by the appropriate transformation. The transformations between the two sets of basis functions have been considered already in Section 7.

Since the 3-j coefficients are necessary for this, as well as for other purposes, we have written programs for their calculation with a 650 IBM electronic computer.

Two programs are available. One is especially adequate for the computation of tables of 3-j coefficients. In this program we have made use of the recursion formulae for the sigmas of Eqs. (8-23, 24) and this contributes considerably to its speed.

Another program has been written as a subroutine to be used in computations of a wider scope where values of 3-j coefficients may be required in the course of the calculations.

All the values are computed in exact form, and given in terms of products of prime numbers or, alternately, as ratios of integers. Further details of the calculations are given immediately preceeding the tables.

## B. MORE GENERAL TREATMENT OF COUPLING COEFFICIENTS

When considering the coupling of angular momenta, the $(j_1 m_1 j_2 m_2 | jm)$ have been defined simply as the coefficients in those linear combinations of product functions

$$|jm) = \sum_{m_1} |j_1 m_1) |j_2 m_2) (j_1 m_1 j_2 m_2 | jm) \tag{8-39}$$

which are also eigenfunctions of the total $J^2$ and $J_z$. In group-theoretical language, the coupling coefficients are the elements of the matrix that reduces the direct product of the irreducible representations $\Gamma_{j_1}$ and $\Gamma_{j_2}$ of the two-dimensional unitary group into its irreducible components, $\Gamma_j$.

We shall now consider this problem more generally, for any group whose irreducible matrix representations are known. The linear combinations of product functions $|\gamma_1 \mu_1) |\gamma_2 \mu_2)$ that transform according to the different irreducible representations of the group in question may be written in the form

$$|\alpha\gamma\mu\rangle = \sum_{\mu_1\mu_2} |\gamma_1\mu_1\rangle\, |\gamma_2\mu_2\rangle\, (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu) \qquad (8\text{-}40)$$

The inverse transformation is

$$|\gamma_1\mu_1\rangle\,|\gamma_2\mu_2\rangle = \sum_{\alpha\gamma\mu} |\alpha\gamma\mu\rangle\,(\alpha\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2) \qquad (8\text{-}41)$$

The extra index $a$ is necessary whenever there is more than one linear combination of product functions that transform according to the irreducible representation $\Gamma$. The number of times that the product representation $\Gamma_i \times \Gamma_j$ contains the irreducible representation $\Gamma_k$ is, according to Eq. (4-27),[*]

$$n_{ij,k} = \frac{1}{h} \sum_R \chi_R^{(i)} \chi_R^{(j)} \chi_R^{(k)*} \qquad (8\text{-}42)$$

The functions $|\alpha\gamma\mu\rangle$ labelled by different values of $a$ may be chosen to be orthonormal, and the coupling coefficients may be considered as the elements of a unitary matrix, so that

$$(\alpha\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2) = (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu)^* \qquad (8\text{-}43)$$

The set of product functions $|\gamma_1\mu_1\rangle\,|\gamma_2\mu_2\rangle$ transform under an operation $R$ of the group according to the direct product matrix $D(R) = \Gamma_1(R) \times \Gamma_2(R)$. The "coupled" functions $|\alpha\gamma\mu\rangle$ transform according to a matrix $D'(R)$ which is in reduced form, that is, it has along its main diagonal the matrices $\Gamma(R)$ of the irreducible representations contained in the direct product $\Gamma_1 \times \Gamma_2$, and zeros elsewhere. The representation matrices are related by a unitary transformation of the form of Eq. (2-16)

$$D'(R) = A^\dagger D(R)\, A \qquad (8\text{-}44)$$

The coupling coefficients are the elements of $A$ and may be determined by solving the above equations. This is the method outlined by Koster[7].

---

[*] If we write $n_{ij,k} = (\Gamma_i\,\Gamma_j\,|\,\Gamma_k)$, these "coefficients of composition" of the group are non-negative integers satisfying symmetry relations of the form

$$(\Gamma_i\Gamma_j|\Gamma_k) = (\Gamma_i^*\Gamma_j^*|\Gamma_k^*) = (\Gamma_j\Gamma_i|\Gamma_k) = (\Gamma_i\Gamma_k^*|\Gamma_j^*)$$

Explicit expressions for the coupling coefficients may be obtained in a more straight forward fashion by use of the projection operators, according to the methods of Section 4. We shall consider first the case when the representation $\Gamma$ is contained only once in the direct product $\Gamma_1 \times \Gamma_2$. We can then write the operator $P_{\mu'\mu}^{(\gamma)}$ of Eq. (4-14) in the form

$$P_{\mu'\mu}^{(\gamma)} = |\gamma\mu'\rangle\langle\gamma\mu| = \frac{d_\gamma}{h} \sum_R (\gamma\mu'|R|\gamma\mu)^* \, R \tag{8-45}$$

In general, when operating on a product function $|\gamma_1\mu_1\rangle\,|\gamma_2\mu_2\rangle$ it generates a linear combination which belongs to the $\mu'$-th row of the irreducible representation $\Gamma$

$$P_{\mu'\mu}^{(\gamma)} \, |\gamma_1\mu_1\rangle \, |\gamma_2\mu_2\rangle = |\gamma\mu'\rangle\,(\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2) \tag{8-46}$$

provided $(\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2) = (\gamma_1\mu_1\gamma_2\mu_2|\gamma\mu)^* \neq 0$. If this does not vanish, we can write

$$|\gamma\mu'\rangle\,(\gamma_1\mu_1\gamma_2\mu_2|\gamma\mu)^* = \frac{d_\gamma}{h} \sum_R (\gamma\mu'|R|\gamma\mu)^* \, R \, |\gamma_1\mu_1\rangle \, |\gamma_2\mu_2\rangle =$$

$$= \frac{d_\gamma}{h} \sum_{\mu_1'\mu_2'} |\gamma_1\mu_1'\rangle\,|\gamma_2\mu_2'\rangle \sum_R (\gamma_1\mu_1'|R|\gamma_1\mu_1)(\gamma_2\mu_2'|R|\gamma_2\mu_2)(\gamma\mu'|R|\gamma\mu)^* \tag{8-47}$$

Comparison with Eq. (8-40) leads to the explicit expression for the coupling coefficients in terms of the matrix elements of the irreducible representations

$$(\gamma_1\mu_1' \, \gamma_2\mu_2' \, |\gamma\mu') =$$

$$\frac{d_\gamma}{h\,(\gamma_1\mu_1\gamma_2\mu_2|\gamma\mu)^*} \sum_R (\gamma_1\mu_1'|R|\gamma_1\mu_1)(\gamma_2\mu_2'|R|\gamma_2\mu_2)(\gamma\mu'|R|\gamma\mu)^* \tag{8-48}$$

By letting $\mu_1'$, $\mu_2'$, and $\mu'$ assume all possible values, while keeping $\mu_1$, $\mu_2$, and $\mu$ fixed, all the coupling coefficients are obtained with the proper phase relations. A common phase factor is still, of course, arbitrary. In the particular case of the two-dimensional unitary group, the expression for the coupling coefficients takes the form

$$(j_1m_1' j_2m_2'|jm') =$$

$$\frac{2j+1}{8\pi^2\,(j_1m_1j_2m_2|jm)^*} \int_R (j_1m_1'|R|j_1m_1)(j_2m_2'|R|j_2m_2)(jm'|R|jm)^* dR \tag{8-49}$$

8-14

which is equivalent to Eq. (17.22) of Wigner[1]. If the explicit expressions for the elements of the rotation matrices, Eqs. (5-9) and (5-10), are introduced in Eq. (8-49) one arrives at the general expression for the coupling coefficients which was given without proof in Section 8, Eq. (8-12). As already mentioned, the above expression defines the coupling coefficients aside from an arbitrary phase factor, $e^{i\phi}$, common to all the $(j_1 m_1 j_2 m_2 | jm)$ for given $j_1, j_2, j$ and all possible values of $m_1$, $m_2$, m. This is usually chosen so that the coupling coefficients for $m_1 = j_1$ are real and positive. Since the integral on the right hand side of Eq. (8-49) is a real number, this choice makes all the coupling coefficients real.

In general, a reducible representation may contain a given irreducible representation $\Gamma$ more than once. We shall therefore express the operator $P^{(\gamma)}_{\mu'\mu}$ symbollically in the general form

$$P^{(\gamma)}_{\mu'\mu} = \sum_\alpha |a\gamma\mu'\rangle (a\gamma\mu| \qquad (8-50)$$

where the index $a$ assumes $n_\gamma$ different values, corresponding to the number of times that the irreducible representation $\gamma$ is contained in the reducible representation under consideration, $n_\gamma$ being given by Eq. (4-27).

If $P^{(\gamma)}_{\mu'\mu}$ operates on a product function, we now have, instead of Eq. (8-47),

$$P^{(\gamma)}_{\mu'\mu} |\gamma_1\mu_1\rangle |\gamma_2\mu_2\rangle = \sum_\alpha |a\gamma\mu'\rangle (a\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2)$$

$$(8-51)$$

$$= \frac{d_\gamma}{h} \sum_{\mu_1'\mu_2'} |\gamma_1\mu_1'\rangle |\gamma_2\mu_2'\rangle \sum_R (\gamma_1\mu_1'|R|\gamma_1\mu_1)(\gamma_2\mu_2'|R|\gamma_2\mu_2)(\gamma\mu'|R|\gamma\mu)^*$$

The (known) sum over the group operations on the right hand side is not in this case proportional to one of the coupling coefficients, but rather a linear combination of $n_\gamma$ of these, since Eq. (8-51) premultiplied by a particular product function $(\gamma_1\mu_1'|\gamma_2\mu_2'|$ gives

$$(\gamma_1\mu_1'\gamma_2\mu_2' | P^{(\gamma)}_{\mu'\mu} | \gamma_1\mu_1\gamma_2\mu_2) =$$

$$= \frac{d_\gamma}{h} \sum_R (\gamma_1\mu_1'|R|\gamma_1\mu_1)(\gamma_2\mu_2'|R|\gamma_2\mu_2)(\gamma\mu'|R|\gamma\mu)^* \qquad (8-52)$$

$$= \sum_\alpha (\gamma_1\mu_1'\gamma_2\mu_2'|a\gamma\mu')(\gamma_1\mu_1\gamma_2\mu_2|a\gamma\mu)^*$$

where use has been made of Eq. (8-43).

Although no simple explicit expression results, there is no difficulty in obtaining the coupling coefficients. As indicated in Section 4, we may operate with $P_{\mu'\mu}^{(\gamma)}$ on $n_\gamma$ different product functions in the form given by Eq. (8-51). If the resulting functions are not orthogonal, an orthonormal set may be constructed from them by any of the usual procedures, or by the methods of Section 4. These may be taken as the $n_\gamma$ desired $|a\gamma\mu\rangle$ functions, and the co-efficients of the $|\gamma_1\mu_1'\rangle\,|\gamma_2\mu_2'\rangle$ are the coupling coefficients $(\gamma_1\mu_1'\gamma_2\mu_2'|a\gamma\mu')$. There is, consequently, considerable arbitrariness in the choice of the $|a\gamma\mu'\rangle$ functions, since any other set of $n_\gamma$ functions $|\beta\gamma\mu'\rangle$ obtained from the $|a\gamma\mu'\rangle$ by a unitary transformation is equally acceptable. The corresponding coupling coefficients are related to the previous ones by

$$(\gamma_1\mu_1'\gamma_2\mu_2'|\beta\gamma\mu') = \sum_a \; (\gamma_1\mu_1'\gamma_2\mu_2'|a\gamma\mu')\,(a|\beta) \qquad\qquad (8\text{-}53)$$

where the coefficients $(a|\beta)$ are the elements of a unitary matrix of order $n_\gamma$. This arbitrariness is the usual one encountered whenever there is a degeneracy; in the present case the $n_\gamma$ functions $|a\gamma\mu\rangle$ all belong to the same eigenvalue (unity) of the $\mu$-th row projection operator $P_{\mu\mu}^{(\gamma)}$.

There are several reasons that make it desirable to introduce further conditions to remove the arbitrariness in the choice of the $|a\gamma\mu\rangle$. The simplest reason concerns the identification of the $n_\gamma$ different functions. For a completely arbitrary choice, $a$ represents only a running index, and conveys no information about $|a\gamma\mu\rangle$. In order to specify this function it is then necessary to list all the coupling coefficients $(\gamma_1\mu_1\gamma_2\mu_2|a\gamma\mu)$ of Eq. (8-40). A better way of identifying a given $|a\gamma\mu\rangle$ is by means of a generating function, that is, in the present case, a certain linear combination of the original product functions such that one of the $P_{\mu\lambda}^{(\gamma)}$ operating on it generates $|a\gamma\mu\rangle$. As indicated in Section 4, the generating function has to be orthogonal to the $n_\gamma-1$ remaining $|a\gamma\lambda\rangle$ functions, and can always be chosen so that it contains at most $n_\gamma$ non-vanishing coefficients.

What is most desirable, in principle, is to arrive at a set of $|a\gamma\mu\rangle$ which are eigen-functions of some operator (or set of operators) in such a way that every value of $a$ cor-responds to a different eigenvalue. Alternatively, it is usually possible to find some symmetry group, different from the one under consideration, such that the coupled functions may be classified according to different irreducible representations of that group.

The preceding remarks are perhaps best illustrated by a simple example. Let us con-sider the reduction of the direct product representation $F_1 \times G_{3/2}$ of the cubic double group $\bar{O}$

$$F_1 \times G_{3/2} = E_{1/2} + E_{5/2} + 2G_{3/2} \qquad (8\text{-}54)$$

which contains twice the $G_{3/2}$ irreducible representation. As basis functions for the $F_1$ representation we may take the angular momentum eigenfunctions $|j_1 m_1\rangle$ for $j_1 = 1$, and similarly for $G_{3/2}$ the functions $|j_2 m_2\rangle$ for $j_2 = 3/2$. The coupled functions may be made eigenfunctions of the total $J^2 = (J_1 + J_2)^2$ thus obtaining two sets of $G_{3/2}$ functions, one corresponding to $j = 3/2$, the other to $j = 5/2$. This is also equivalent to classifying the coupled functions according to the irreducible representations of the rotation group $R_3$.

Similarly, the direct product of the representation F of the tetrahedral group T with itself

$$F \times F = A + E + 2F \qquad (8\text{-}55)$$

contains the representation F twice. T is a subgroup of O and we can choose sets of functions of type $F_1$ in O as basis functions F' for the group T. The corresponding direct product in O is

$$F_1 \times F_1 = A_1 + E + F_1 + F_2 \qquad (8\text{-}56)$$

so that the two sets of F coupled functions of the group T can be classified, one as $F_1$, the other as $F_2$, under O.

### ORTHOGONALITY RELATIONS

These are simply an expression of the unitary nature of the transformation (8-40, 41)

$$\sum_{\alpha\gamma\mu} (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu)(\alpha\gamma\mu|\gamma_1\mu_1'\gamma_2\mu_2')$$

$$= \sum_{\alpha\gamma\mu} (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu)(\gamma_1\mu_1'\gamma_2\mu_2'|\alpha\gamma\mu)^* = \delta(\mu_1,\mu_1')\,\delta(\mu_2,\mu_2') \qquad (8\text{-}57)$$

$$\sum_{\mu_1\mu_2} (\alpha\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2)(\gamma_1\mu_1\gamma_2\mu_2|\alpha'\gamma'\mu')$$

$$= \sum_{\mu_1\mu_2} (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu)^*(\gamma_1\mu_1\gamma_2\mu_2|\alpha'\gamma'\mu') = \delta(\alpha,\alpha')\,\delta(\gamma,\gamma')\,\delta(\mu,\mu') \qquad (8\text{-}58)$$

## COUPLING RULES FOR THE $(\gamma\mu'|R|\gamma\mu)$

The coupling rules for the elements of the representation matrices may be obtained by the same arguments used in the case of the rotation matrices, Eqs. (8-30) to (8-33). In the general case we have

$$(\gamma_3\mu_3'|R|\gamma_3\mu_3) =$$

$$= \sum_{\mu_1,\mu_2,\mu_1',\mu_2'} \sum \cdot (a_3\gamma_3\mu_3'|\gamma_1\mu_1'\gamma_2\mu_2') (\gamma_1\mu_1\gamma_2\mu_2|a_3\gamma_3\mu_3) (\gamma_1\mu_1'|R|\gamma_1\mu_1) (\gamma_2\mu_2'|R|\gamma_2\mu_2)$$

$$(8\text{-}59)$$

$$(\gamma_1\mu_1'|R|\gamma_1\mu_1) (\gamma_2\mu_2'|R|\gamma_2\mu_2)$$

$$= \sum_{a_3\gamma_3} \sum_{\mu_3,\mu_3'} (\gamma_1\mu_1'\gamma_2\mu_2'|a_3\gamma_3\mu_3') (a_3\gamma_3\mu_3|\gamma_1\mu_1\gamma_2\mu_2) (\gamma_3\mu_3'|R|\gamma_3\mu_3)$$

$$(8\text{-}60)$$

As in the previous formulae, the coefficients $(a_3\gamma_3\mu_3|\gamma_1\mu_1\gamma_2\mu_2)$ may be replaced by $(\gamma_1\mu_1\gamma_2\mu_2|a_3\gamma_3\mu_3)^*$.

# 9. COUPLING COEFFICIENTS FOR THE POINT GROUPS

The coupling coefficients for the point groups are easily obtained from the results of the previous Section.

If only one-dimensional representations are involved, the coupling coefficients may be taken to be unity if $\Gamma_1 \times \Gamma_2 = \Gamma$, and zero otherwise. They are thus identical with the $n_{ij,k}$ of Eq. (8-42) and are easily obtained from the rules for representation multiplication.

For the degenerate representations, they may be obtained from Eqs. (8-48) or (8-52) and the irreducible representation matrices. The coupling coefficients given in this Section correspond to the choice of representation matrices given in Section 6, Tables 6-3 and 6-4.

*GROUPS* $C_n$, $C_{nh}$, *AND* $S_{2n}$

The representations of the groups $C_n$, $C_{nh}$, and $S_{2n}$ are all one-dimensional, and the coupling coefficients may be chosen to be one or zero.

Thus, for example, for the $C_n$ groups, the multiplication rule is

$$\Gamma_{\mu_1} \times \Gamma_{\mu_2} = \Gamma_{\mu_3} \tag{9-1}$$

where

$$\mu_3 = \mu_1 + \mu_2 \pm n \tag{9-2}$$

the plus or minus sign being chosen so that

$$-n/2 < \mu_3 \leqslant n/2 \tag{9-3}$$

Accordingly, the coupling coefficients are of the form

$$(\gamma_1\mu_1\gamma_2\mu_2|\gamma_3\mu_3) = \delta(\mu_3, \mu_1 + \mu_2 \pm n) \tag{9-4}$$

For the groups $C_{nh}$ ($n$ even) and $S_{2n}$ ($n$ odd) we have, in addition, the multiplication rule

$$g \times g = u \times u = g$$
$$g \times u = u \tag{9-5}$$

and the coupling coefficients are

$$(\sigma_1 \gamma_1 \mu_1, \ \sigma_2 \gamma_2 \mu_2 | \sigma_3 \gamma_3 \mu_3) = \delta (\mu_3, \ \mu_1 + \mu_2 \pm n) \ \delta \ (\sigma_3, \ \sigma_1 \pm \sigma_2) \tag{9-6}$$

where, as indicated previously, $\sigma = 1$ for functions of even parity, and $\sigma = 0$ for those of odd parity.

For the groups $C_{nh}$ (n odd) and $S_{2n}$ (n even), isomorphous with $C_{2n}$, the results for $C_n$ apply, with $\underline{n}$ replaced by $2n$.

## GROUPS $D_n$, $C_{nv}$ *(n even)*

The coupling coefficients associated with only one-dimensional representations may be taken as unity or zero. The multiplication rules for these are symbolized as follows

$$A \times A = B \times B = A$$
$$A \times B = B \tag{9-7}$$

$$(1) \times (1) = (2) \times (2) = (1)$$
$$(1) \times (2) = (2) \tag{9-8}$$

We shall label the basis functions $|\gamma\mu\rangle$ for the two-dimensional representations $E_\gamma$ as $|\gamma\rangle$ or $|-\gamma\rangle$, for brevity. The product of these and one-dimensional representations are always of the form

$$A \times E_\gamma = E_\gamma \qquad B \times E_\gamma = E_{n/2 \ -\gamma} \tag{9-9}$$

The coupling coefficients are given as follows

$$\text{o}$$

TABLE 9-1

| $A_1 \times E_\gamma$ | $E_\gamma$ | | $A_2 \times E_\gamma$ | $E_\gamma$ | |
|---|---|---|---|---|---|
| | $\|\gamma)$ | $\|-\gamma)$ | | $\|\gamma)$ | $\|-\gamma)$ |
| $\|A_1)\,\|\gamma)$ | 1 | 0 | $\|A_2)\,\|\gamma)$ | 1 | 0 |
| $\|A_1)\,\|-\gamma)$ | 0 | 1 | $\|A_2)\,\|-\gamma)$ | 0 | $-1$ |

| $B_1 \times E_\gamma$ | $E_{n/2\,-\gamma}$ | | $B_2 \times E_\gamma$ | $E_{n/2\,-\gamma}$ | |
|---|---|---|---|---|---|
| | $\|\frac{n}{2}-\gamma)$ | $\|-\frac{n}{2}+\gamma)$ | | $\|\frac{n}{2}-\gamma)$ | $\|-\frac{n}{2}+\gamma)$ |
| $\|B_1)\,\|\gamma)$ | 0 | 1 | $\|B_2)\,\|\gamma)$ | 0 | 1 |
| $\|B_1)\,\|-\gamma)$ | $(-1)^{2\gamma}$ | 0 | $\|B_2)\,\|-\gamma)$ | $-(-1)^{2\gamma}$ | 0 |

In these tables, as well as in those to follow later, the coupling coefficient $(\gamma_1\mu_1,\gamma_2\mu_2|\gamma\mu)$ appears in the row labelled by $|\mu_1)\,|\mu_2)$ and the column labelled by $|\mu)$.

In general, the product of two degenerate representations is of the form

$$E_{\gamma_1} \times E_{\gamma_2} = E_{\gamma_1+\gamma_2} + E_{\gamma_1-\gamma_2} \tag{9-10}$$

However, if $\gamma_1 + \gamma_2 = n/2$ we have instead of $E_{\gamma_1+\gamma_2}$ two one-dimensional representations, $B_1$ and $B_2$. Similarly, if $\gamma_1-\gamma_2 = 0$, the place of $E_{\gamma_1-\gamma_2}$ is taken by the two-one dimensional representations $A_1$ and $A_2$. The coupling coefficients for the different possible values of $\gamma_1 + \gamma_2$ and $\gamma_1 - \gamma_2$ (assuming $\gamma_1 \geqslant \gamma_2$) are given in Table 9-2.

## TABLE 9-2

| $E_{\gamma_1} \times E_{\gamma_2}$ | $0 < \gamma_1 + \gamma_2 < n/2$ | | $\gamma_1 + \gamma_2 = n/2$ | | $n/2 < \gamma_1 + \gamma_2 < n$ | |
|---|---|---|---|---|---|---|
| | $E_{\gamma_1 + \gamma_2}$ | | $B_1 + B_2$ | | $E_{n-\gamma_1-\gamma_2}$ | |
| | $|\gamma_1+\gamma_2\rangle$ | $|-\gamma_1-\gamma_2\rangle$ | $|B_1\rangle$ | $|B_2\rangle$ | $|n-\gamma_1-\gamma_2\rangle$ | $|-n+\gamma_1+\gamma_2\rangle$ |
| $|\gamma_1\rangle\,|\gamma_2\rangle$ | 1 | 0 | $\sqrt{1/2}$ | $\sqrt{1/2}$ | 0 | $(-1)^{2(\gamma_1+\gamma_2)}$ |
| $|-\gamma_1\rangle\,|-\gamma_2\rangle$ | 0 | 1 | $\sqrt{1/2}$ | $-\sqrt{1/2}$ | 1 | 0 |

| $E_{\gamma_1} \times E_{\gamma_2}$ | $0 < \gamma_1 - \gamma_2 < n/2$ | | $\gamma_1 - \gamma_2 = 0$ | |
|---|---|---|---|---|
| | $E_{\gamma_1 - \gamma_2}$ | | $A_1 + A_2$ | |
| | $|\gamma_1-\gamma_2\rangle$ | $|-\gamma_1+\gamma_2\rangle$ | $|A_1\rangle$ | $|A_2\rangle$ |
| $|\gamma_1\rangle\,|-\gamma_2\rangle$ | 1 | 0 | $\sqrt{1/2}$ | $\sqrt{1/2}$ |
| $|-\gamma_1\rangle\,|\gamma_2\rangle$ | 0 | $(-1)^{2\gamma_1}$ | $(-1)^{2\gamma_1}/\sqrt{2}$ | $-(-1)^{2\gamma_1}/\sqrt{2}$ |

## GROUPS $D_n$ AND $C_{nv}$ (n odd)

The same results as for $\underline{n}$ even are valid, except when the complex representations $B_1$ and $B_2$ are involved. In particular, it should be noticed that, unlike the case of $\underline{n}$ even, one now has

$$B_1 \times B_1 = B_2 \times B_2 = A_2$$
$$B_1 \times B_2 = A_1 \tag{9-11}$$

In addition, the coupling coefficients involving $B_1$ or $B_2$ and the doubly degenerate representations cannot be chosen to be all real. The coupling coefficients which differ from those for $\underline{n}$ even are

$$(B_1 B_1 | A_2) = (B_2 B_2 | A_2) = (B_1 B_2 | A_1) = 1$$
$$(B_1 B_1 | A_1) = (B_2 B_2 | A_1) = (B_1 B_2 | A_2) = 0 \tag{9-12}$$

and those in the following Table 9-3.

TABLE 9-3

| $B_1 \times E_\gamma$ | $E_{\frac{n}{2}-\gamma}$ | |
|---|---|---|
| | $\lvert\frac{n}{2}-\gamma\rangle$ | $\lvert-\frac{n}{2}+\gamma\rangle$ |
| $\lvert B_1\rangle\ \lvert\gamma\rangle$ | 0 | 1 |
| $\lvert B_1\rangle\ \lvert-\gamma\rangle$ | $i(-1)^{2\gamma}$ | 0 |

| $B_2 \times E_\gamma$ | $E_{\frac{n}{2}-\gamma}$ | |
|---|---|---|
| | $\lvert\frac{n}{2}-\gamma\rangle$ | $\lvert-\frac{n}{2}+\gamma\rangle$ |
| $\lvert B_2\rangle\ \lvert\gamma\rangle$ | 0 | 1 |
| $\lvert B_2\rangle\ \lvert-\gamma\rangle$ | $-i(-1)^{2\gamma}$ | 0 |

| $E_{\gamma_1} \times E_{\gamma_2}$ | $\gamma_1 + \gamma_2 = n/2$ | |
|---|---|---|
| | $B_1 + B_2$ | |
| | $\lvert B_1\rangle$ | $\lvert B_2\rangle$ |
| $\lvert\gamma_1\rangle\ \lvert\gamma_2\rangle$ | $\sqrt{1/2}$ | $\sqrt{1/2}$ |
| $\lvert-\gamma_1\rangle\ \lvert-\gamma_2\rangle$ | $i/\sqrt{2}$ | $-i/\sqrt{2}$ |

### GROUPS $D_{nh}$ *(n even)* AND $D_{nd}$ *(n odd)*

The same results as for $D_n$ apply, with the additional rule

$$g \times g \times u \times u = g$$
$$u \times g = u \tag{9-13}$$

### GROUPS $D_{nh}$ *(n odd)* AND $D_{nd}$ *(n even)*

The same results as for $D_n$ ( $\underline{n}$ even) are valid, with 2n in place of $\underline{n}$.

### GROUP O

If the elements of the representation matrices given in Table 6-4 are introduced in Eq. (8-48) and the summations over the values of the angles $a$ and $y$ are performed, one can easily arrive at an expression for the coupling coefficients which, for the choice of functions referred to the cubic set of axes, takes the form

$$\circ \, (\gamma_1\mu_1'\gamma_2\mu_2' \,|\, \alpha\gamma\mu') = \frac{d_\gamma}{6} \; \frac{1}{(\gamma_1\mu_1\gamma_2\mu_2\,|\,\alpha\gamma\mu)}$$

$$\times \left[ c(0)_{\mu_1'\mu_1} \, c(0)_{\mu_2'\mu_2} \, c(0)_{\mu'\mu} \; + \; c(\pi)_{\mu_1'\mu_1} c(\pi)_{\mu_2'\mu_2} c(\pi)_{\mu'\mu} \right. \tag{9-14}$$

$$\left. + \; \frac{1}{16} \, c(\pi/2)_{\mu_1'\mu_1} \; c(\pi/2)_{\mu_2'\mu_2} \; c(\pi/2)_{\mu'\mu} \right]$$

where the coefficients $c(\beta)$ are those which appear in Eqs. (7-34, 35) and are given in Table 7-1.

For the choice of representation matrices made when the basis functions are referred to the trigonal set of axes (see also Eqs. (7-39, 40)) a similar expression is obtained

$$(\gamma_1\mu_1'\gamma_2\mu_2' \,|\, \alpha\gamma\mu') = \frac{d_\gamma}{8} \; \frac{1}{(\gamma_1\mu_1\gamma_2\mu_2\,|\,\alpha\gamma\mu)}$$

$$\times \left[ c(0)_{\mu_1'\mu_1} \, c(0)_{\mu_2'\mu_2} \, c(0)_{\mu'\mu} \; + \; c(\pi)_{\mu_1'\mu_1} \, c(\pi)_{\mu_2'\mu_2} c(\pi)_{\mu'\mu} \right. \tag{9-15}$$

$$\left. + \; \frac{1}{9} \, (-1)^{\mu_1+\mu_2-\mu} \left( c^+(r)_{\mu_1'\mu_1} c^+(r)_{\mu_2'\mu_2} c^+(r)_{\mu'\mu} \; + \; c^-(r)_{\mu_1'\mu_1} c^-(r)_{\mu_2'\mu_2} c^-(r)_{\mu'\mu} \right) \right]$$

where the coefficients $c(\beta)$ are those of Eqs. (7-41, 42) and are given in Table 7-3.

The coupling coefficients for the functions referred to the cubic set of axes have been reproduced in the Tables. In the products

$$F_1 \times G_{3/2} = E_{1/2} + E_{5/2} + 2G_{3/2}$$

$$F_2 \times G_{3/2} = E_{1/2} + E_{5/2} + 2G_{3/2} \qquad\qquad . \tag{9-16}$$

$$G_{3/2} \times G_{3/2} = A_1 + A_2 + E + 2F_1 + 2F_2$$

some irreducible representations are contained twice and therefore Eqs. (9-14) and (9-15) require a slight modification, according to Eq. (8-52).

As indicated in the previous Section, the choice of the two sets of basis functions of the same symmetry in the product may be done according to different criteria. If we choose

as basis functions for the original $F_1$ the $|jm)$ functions for $j = 1$, and for the $G_{3/2}$ the $|jm)$ functions for $j = 3/2$, we can choose linear combinations of product functions which are eigenfunctions of the total $J^2$, so that

$$F_1 (j_1 = 1) \times G_{3/2} (j_2 = 3/2) =$$
$$= E_{1/2}(J = 1/2) + E_{5/2}(J = 5/2) + G_{3/2}(J = 3/2) + G_{3/2}(J = 5/2) \qquad (9\text{-}17)$$

and similarly

$$G_{3/2}(j_1 = 3/2) \times G_{3/2}(j_2 = 3/2) =$$

$$= A_1(J = 0) + A_2(J = 3) + E(J = 2) + F_1(J =1) + F_1(J = 3) + F_2(J = 2) + F_2(J =3)$$
$$(9\text{-}18)$$

The corresponding coupling coefficients are given for convenience in Table 9-4.

TABLE 9-4

| $F_1 \times G_{3/2}$ | $E_{1/2}$ | | $G_{3/2}$ | | | | $E_{5/2}$ | | $G_{3/2}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\|1/2)$ | $\|-1/2)$ | $\|3/2)$ | $\|1/2)$ | $\|-1/2)$ | $\|-3/2)$ | $\|5/2)$ | $\|-5/2)$ | $\|3/2)$ | $\|1/2)$ | $\|-1/2)$ | $\|-3/2)$ |
| $\|1) \|3/2)$ | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/6}$ | 0 | 0 | 0 | 0 | $\sqrt{5/6}$ |
| $\|1) \|1/2)$ | 0 | 0 | $\sqrt{2/5}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/2}$ | $-\sqrt{1/10}$ | 0 | 0 | 0 |
| $\|1) \|-1/2)$ | $\sqrt{1/6}$ | 0 | 0 | $\sqrt{8/15}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{3/10}$ | 0 | 0 |
| $\|1) \|-3/2)$ | 0 | $\sqrt{1/2}$ | 0 | 0 | $\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/10}$ | 0 |
| $\|0) \|3/2)$ | 0 | 0 | $-\sqrt{3/5}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/3}$ | $-\sqrt{1/15}$ | 0 | 0 | 0 |
| $\|0) \|1/2)$ | $-\sqrt{1/3}$ | 0 | 0 | $-\sqrt{1/15}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{3/5}$ | 0 | 0 |
| $\|0) \|-1/2)$ | 0 | $-\sqrt{1/3}$ | 0 | 0 | $\sqrt{1/15}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{3/5}$ | 0 |
| $\|0) \|-3/2)$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{3/5}$ | $-\sqrt{1/3}$ | 0 | 0 | 0 | 0 | $\sqrt{1/15}$ |
| $\|-1) \|3/2)$ | $\sqrt{1/2}$ | 0 | 0 | $-\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/10}$ | 0 | 0 |
| $\|-1) \|1/2)$ | 0 | $\sqrt{1/6}$ | 0 | 0 | $-\sqrt{8/15}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{3/10}$ | 0 |
| $\|-1) \|-1/2)$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{2/5}$ | $-\sqrt{1/2}$ | 0 | 0 | 0 | 0 | $\sqrt{1/10}$ |
| $\|-1) \|-3/2)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/6}$ | $-\sqrt{5/6}$ | 0 | 0 | 0 |

## $F_2 \times G_{3/2}$

| $F_2 \times G_{3/2}$ | $E_{5/2}$ | | $G_{3/2}$ | | | | $E_{1/2}$ | | $G_{3/2}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lvert 5/2\rangle$ | $\lvert{-}5/2\rangle$ | $\lvert 3/2\rangle$ | $\lvert 1/2\rangle$ | $\lvert{-}1/2\rangle$ | $\lvert{-}3/2\rangle$ | $\lvert 1/2\rangle$ | $\lvert{-}1/2\rangle$ | $\lvert 3/2\rangle$ | $\lvert 1/2\rangle$ | $\lvert{-}1/2\rangle$ | $\lvert{-}3/2\rangle$ |
| $\lvert{-}1\rangle\lvert 3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/6}$ | 0 | 0 | $\sqrt{5/6}$ | 0 | 0 |
| $\lvert{-}1\rangle\lvert 1/2\rangle$ | 0 | 0 | 0 | 0 | $\sqrt{2/5}$ | 0 | 0 | $\sqrt{1/2}$ | 0 | 0 | $-\sqrt{1/10}$ | 0 |
| $\lvert{-}1\rangle\lvert{-}1/2\rangle$ | $\sqrt{1/6}$ | 0 | 0 | 0 | 0 | $-\sqrt{8/15}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{3/10}$ |
| $\lvert{-}1\rangle\lvert{-}3/2\rangle$ | 0 | $\sqrt{1/2}$ | $-\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/10}$ | 0 | 0 | 0 |
| $\lvert 2\rangle\lvert 3/2\rangle$ | 0 | 0 | 0 | 0 | $-\sqrt{3/5}$ | 0 | 0 | $\sqrt{1/3}$ | 0 | 0 | $-\sqrt{1/15}$ | 0 |
| $\lvert 2\rangle\lvert 1/2\rangle$ | $-\sqrt{1/3}$ | 0 | 0 | 0 | 0 | $\sqrt{1/15}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{3/5}$ |
| $\lvert 2\rangle\lvert{-}1/2\rangle$ | 0 | $-\sqrt{1/3}$ | $-\sqrt{1/15}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{3/5}$ | 0 | 0 | 0 |
| $\lvert 2\rangle\lvert{-}3/2\rangle$ | 0 | 0 | 0 | $\sqrt{3/5}$ | 0 | 0 | $\sqrt{1/3}$ | 0 | 0 | $\sqrt{1/15}$ | 0 | 0 |
| $\lvert 1\rangle\lvert 3/2\rangle$ | $\sqrt{1/2}$ | 0 | 0 | 0 | 0 | $\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/10}$ |
| $\lvert 1\rangle\lvert 1/2\rangle$ | 0 | $\sqrt{1/6}$ | $\sqrt{8/15}$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{3/10}$ | 0 | 0 | 0 |
| $\lvert 1\rangle\lvert{-}1/2\rangle$ | 0 | 0 | 0 | $-\sqrt{2/5}$ | 0 | 0 | $\sqrt{1/2}$ | 0 | 0 | $\sqrt{1/10}$ | 0 | 0 |
| $\lvert 1\rangle\lvert{-}3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/6}$ | 0 | 0 | $-\sqrt{5/6}$ | 0 |

## $G_{3/2} \times G_{3/2}$

| $G_{3/2}\times G_{3/2}$ | $A_1$ | $F_1$ | | | $E$ | | $F_2$ | | | $A_2$ | $F_1$ | | | $F_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lvert 0\rangle$ | $\lvert 1\rangle$ | $\lvert 0\rangle$ | $\lvert{-}1\rangle$ | $\lvert 0\rangle$ | $\lvert 2\rangle$ | $\lvert 1\rangle$ | $\lvert 2\rangle$ | $\lvert{-}1\rangle$ | $\lvert 2\rangle$ | $\lvert 1\rangle$ | $\lvert 0\rangle$ | $\lvert{-}1\rangle$ | $\lvert{-}1\rangle$ | $\lvert 2\rangle$ | $\lvert 1\rangle$ |
| $\lvert 3/2\rangle\lvert 3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{5/8}$ | $\sqrt{3/8}$ | 0 | 0 |
| $\lvert 3/2\rangle\lvert 1/2\rangle$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/4}$ | 0 | $\sqrt{9/20}$ | 0 | $\sqrt{1/4}$ | 0 | 0 | 0 | 0 | $\sqrt{1/20}$ | 0 |
| $\lvert 3/2\rangle\lvert{-}1/2\rangle$ | 0 | $\sqrt{3/10}$ | 0 | 0 | 0 | 0 | $\sqrt{1/2}$ | 0 | 0 | 0 | $\sqrt{3/40}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/8}$ |
| $\lvert 3/2\rangle\lvert{-}3/2\rangle$ | $\sqrt{1/4}$ | 0 | $\sqrt{9/20}$ | 0 | $\sqrt{1/4}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/20}$ | 0 | 0 | 0 | 0 |
| $\lvert 1/2\rangle\lvert 3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/4}$ | 0 | $-\sqrt{1/20}$ | 0 | $-\sqrt{1/4}$ | 0 | 0 | 0 | 0 | $\sqrt{9/20}$ | 0 |
| $\lvert 1/2\rangle\lvert 1/2\rangle$ | 0 | $-\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{9/40}$ | 0 | 0 | 0 | 0 | $-\sqrt{3/8}$ |
| $\lvert 1/2\rangle\lvert{-}1/2\rangle$ | $-\sqrt{1/4}$ | 0 | $-\sqrt{1/20}$ | 0 | $\sqrt{1/4}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{9/20}$ | 0 | 0 | 0 | 0 |
| $\lvert 1/2\rangle\lvert{-}3/2\rangle$ | 0 | 0 | 0 | $\sqrt{3/10}$ | 0 | 0 | 0 | 0 | $\sqrt{1/2}$ | 0 | 0 | 0 | $\sqrt{3/40}$ | $-\sqrt{1/8}$ | 0 | 0 |
| $\lvert{-}1/2\rangle\lvert 3/2\rangle$ | 0 | $\sqrt{3/10}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/2}$ | 0 | 0 | 0 | $\sqrt{3/40}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/8}$ |
| $\lvert{-}1/2\rangle\lvert 1/2\rangle$ | $\sqrt{1/4}$ | 0 | $-\sqrt{1/20}$ | 0 | $-\sqrt{1/4}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{9/20}$ | 0 | 0 | 0 | 0 |
| $\lvert{-}1/2\rangle\lvert{-}1/2\rangle$ | 0 | 0 | 0 | $-\sqrt{2/5}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{9/40}$ | $-\sqrt{3/8}$ | 0 | 0 |
| $\lvert{-}1/2\rangle\lvert{-}3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/4}$ | 0 | $-\sqrt{1/20}$ | 0 | $\sqrt{1/4}$ | 0 | 0 | 0 | 0 | $\sqrt{9/20}$ | 0 |
| $\lvert{-}3/2\rangle\lvert 3/2\rangle$ | $-\sqrt{1/4}$ | 0 | $\sqrt{9/20}$ | 0 | $-\sqrt{1/4}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{1/20}$ | 0 | 0 | 0 | 0 |
| $\lvert{-}3/2\rangle\lvert 1/2\rangle$ | 0 | 0 | 0 | $\sqrt{3/10}$ | 0 | 0 | 0 | 0 | $-\sqrt{1/2}$ | 0 | 0 | 0 | $\sqrt{3/40}$ | $-\sqrt{1/8}$ | 0 | 0 |
| $\lvert{-}3/2\rangle\lvert{-}1/2\rangle$ | 0 | 0 | 0 | 0 | 0 | $-\sqrt{1/4}$ | 0 | $\sqrt{9/20}$ | 0 | $-\sqrt{1/4}$ | 0 | 0 | 0 | 0 | $\sqrt{1/20}$ | 0 |
| $\lvert{-}3/2\rangle\lvert{-}3/2\rangle$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{5/8}$ | 0 | 0 | 0 | 0 | $\sqrt{3/8}$ |

The coupling coefficients chosen there for $F_2 \times G_{3/2}$ are related to those for $F_1 \times G_{3/2}$ by simple symmetry relations.

This choice of coupling coefficients is not the one we have preferred in the final Tables. In these, the product functions in $G_{3/2} \times G_{3/2}$ have been classified as symmetric or antisymmetric with respect to a simple linear transformation of the original functions

$$\widetilde{\Psi}'_{3/2} = \widetilde{\Psi}_{3/2} \, A \tag{9-19}$$

where the matrix $A$ is

$$A = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{9-20}$$

(This may be recognized as the matrix of coupling coefficients for the product $A_2 \times G_{3/2} = G_{3/2}$) The product functions of $G_{3/2} \times G_{3/2}$ which are symmetric under the transformation belong to $A_1$, $A_2$, $F_1$, and $F_2$, while the antisymmetric belong to $E$, $F_1$, and $F_2$. The $F_1$ or $F_2$ symmetric functions are designated in the tables as $F_1^{(+)}$ and $F_2^{(+)}$, while the antisymmetric as $F_1^{(-)}$ and $F_2^{(-)}$. It may also be noticed that this choice leads to simpler results for the coupling coefficients.

The coupling coefficients for the $G_{3/2}$ functions in the products $F_1 \times G_{3/2}$ and $F_2 \times G_{3/2}$ have been then obtained from the previous ones in such a way that they satisfy the simplest symmetry relations. We shall consider this point in more detail in the section dealing with the symmetrized coupling coefficients.

The relation between the $F_1^{(+)}$ or $F_2^{(-)}$ and those of Eq. (9-18) is

$$F_1^{(+)} = \left[ F_1(J = 1) + 2F_1(J = 3) \right] / \sqrt{5}$$
$$F_1^{(-)} = \left[ 2F_1(J = 1) - F_1(J = 3) \right] / \sqrt{5} \tag{9-21}$$

Similarly the $G_{3/2}^{(+)}$ and $G_{3/2}^{(-)}$ of the product $F_1 \times G_{3/2}$ are related to those in Eq. (9-17) in the form

$$G_{3/2}^{(+)} = \left[ G_{3/2}(J = 3/2) + 2G_{3/2}(J = 5/2) \right] / \sqrt{5}$$
$$G_{3/2}^{(-)} = \left[ 2G_{3/2}(J = 3/2) - G_{3/2}(J = 5/2) \right] / \sqrt{5} \tag{9-22}$$

9-9

*GROUP* **T**

The coupling coefficients for T may be obtained from those for the group O with some slight modifications. With our choice of representations the coupling coefficients involving A, F, and $E_{1/2}$ are the same as those for the group O, taking into account the correlation

$$
\begin{aligned}
A_1, A_2 &\longrightarrow A \\
F_1, F_2 &\longrightarrow F \\
E_{1/2}, E_{5/2} &\longrightarrow E_{1/2}
\end{aligned}
\tag{9-23}
$$

The choice of representation matrices for E and $G_{3/2}$ of the group O is such that the basis functions for $E_a$, $E_b$, $G_a$, and $G_b$ of the group T are obtained from them by a transformation, Eq. (7-45)

$$
\widetilde{\Psi}_T = \widetilde{\Psi}_O A
\tag{9-24}
$$

The matrix $C_T$ whose elements are the coupling coefficients $(\gamma_1\mu_1\gamma_2\mu_2|a\gamma_3\mu_3)_T$ for the group T is obtained from the corresponding matrix $C_O$ for the group O by means of the transformation

$$
C_T = \left[ A^{(1)} \times A^{(2)} \right]^\dagger C_O A^{(3)}
\tag{9-25}
$$

where the matrices $A^{(\gamma)}$ for the E and $G_{3/2}$ representations are those given in Eqs. (6-17) and (6-18). For the remaining representations the $A^{(\gamma)}$ are unit matrices.

It should be remarked that the coupling coefficients involving $E_a$, $E_b$, $G_a$, and $G_b$, cannot be chosen to be all real, as in the previous case of the $D_n$ groups with $n$ odd. This is due to the fact that the representations in question have complex characters or, in other words, are not equivalent to their complex conjugate representations.

*GROUP* **T**$_d$

Since the representation matrices have been chosen to be identical with those for the group O, the coupling coefficients are also the same for both groups.

*GROUPS* **T**$_h$ *AND* **O**$_h$

These are direct product groups, and the coupling coefficients are obtained from those for T and O taking into account the additional parity multiplication rule.

# 10. IRREDUCIBLE SPHERICAL TENSORS

When considering atomic wave functions it is often preferable to operate in spherical rather than cartesian coordinates. The spherical basis functions appear in a natural way as basis functions of a representation where $J$ and $J_z$ are diagonal. This is intimately related to their transformation properties under rotations of the coordinate system. Thus, for example, spherical harmonics with different $j$ values are basis for different irreducible representations of the rotation group in three dimensions, $R_3$. Similarly, different $m$ values correspond to different irreducible representations of the group of rotations about the z-axis.

Cartesian coordinates (or momenta) and their products afford bases for representations which are, in general, reducible. For example, although x, y, and z themselves are basis of an irreducible representation, $(j = 1)$, only the appropriate linear combinations

$$- (x + iy)/\sqrt{2} = (4\pi/3)^{\frac{1}{2}} r Y_1^1 ,$$
$$z = (4\pi/3)^{\frac{1}{2}} r Y_1^0 ,$$
$$(x - iy)/\sqrt{2} = (4\pi/3)^{\frac{1}{2}} r Y_1^{-1} \tag{10-1}$$

diagonalize $J_z$.

The six products $x^2$, $y^2$, $z^2$, xy, xz, and yz afford a reducible representation. There is a linear combination

$$x^2 + y^2 + z^2 \equiv r^2 \tag{10-2}$$

which is invariant under rotations, as $Y_0^0$, while five other appropriate linear combinations will transform as the second order spherical harmonics, $Y_2^m$. Similarly, we may consider the nine products of the cartesian components of two vectors. The linear combination

$$x_1 x_2 + y_1 y_2 + z_1 z_2 \equiv (\vec{r}_1 \cdot \vec{r}_2) \tag{10-3}$$

is a scalar and remains invariant under rotations. The three linear combinations

$$x_1y_2 - y_1x_2$$

$$y_1z_2 - z_1y_2 \qquad (10\text{-}4)$$

$$z_1x_2 - x_1z_2$$

afford a basis for the $j = 1$ representation, just as $Y_1^m$. The five remaining (independent) linear combinations afford a basis for the $j = 2$ representation, as the $Y_2^m$ spherical harmonics.

When we come to consider the quantum mechanical operators associated with functions of the coordinates or momenta the preceeding considerations about their transformation properties are also valid. In addition, we shall find that the matrices of operators in spherical basis are also simpler than in cartesian. A know example is that of the angular momentum operators themselves. For p-states, $(j = 1)$, the matrices for $J_x$, $J_y$, and $J_z$ are

$$J_x = \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{pmatrix} \quad ; \quad J_y = \begin{pmatrix} 0 & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & i/\sqrt{2} & 0 \end{pmatrix} \quad ; \quad J_z = \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}$$

$$(10\text{-}5)$$

The corresponding angular momentum operators in the spherical system are

$$J_1 = -(J_x + iJ_y) / \sqrt{2} \; ; \qquad J_0 = J_z; \qquad J_{-1} = (J_x - iJ_y) / \sqrt{2} \qquad (10\text{-}6)$$

and the matrices for p-states

$$J_1 = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} \quad ; \quad J_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad ; \quad J_{-1} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad (10\text{-}7)$$

Similarly, we have seen (Eq. 8-37) that the only non-vanishing matrix elements of the spherical hamonics are of the form

$$( \ell \, m \mid Y_L^M \mid \ell', \, m\text{-}M)$$

so that there are only elements along a line parallel to the main diagonal.

It should be noticed that the matrices of the operators in the spherical basis are not Hermitian. While for a Hermitian operator ( $H = H^\dagger$ ) such as $J_x$, we have

$$(\ell\, m|\, J_x\, |\, \ell'm') = (\ell'm'|\, J_x\, |\, \ell m)^*  \qquad (10\text{-}8)$$

for an "irreducible tensor operator" in the spherical basis, such as $Y_L^M$ , we have

$$(\ell\, m|\, Y_L^M\, |\, \ell'm') = (-1)^M\, (\ell'm'|\, Y_L^{-M}\, |\, \ell m)^*  \qquad (10\text{-}9)$$

or, more generally

$$(T_L^M)^\dagger = (-1)^M\, T_L^{-M}  \qquad (10\text{-}10)$$

(This merely reflects the fact that the corresponding functions are not real. Compare (10-10) with the definition $(Y_L^M)^* = (-1)^M\, Y_L^{-M}$ adopted for the spherical harmonics).

With the preceeding considerations in mind we may now define an "irreducible tensor operator" of rank L as a set of $2L + 1$ functions (operators) which transform under rotations of the coordinate axes in the same way as the spherical harmonics of order L:

$$R\, T_L^M\, R^{-1} = \sum_{M'} D_{M'M}^L (\alpha\beta\gamma)\, T_L^{M'}  \qquad (10\text{-}11)$$

(Remember that if the basis functions $\psi$ are changed by the transformation R in the form $\psi \to R\psi$, an operator or matrix is changed in the form $T \to R\, T\, R^{-1}$. See Eq. 3-7).

Alternatively, it may be defined by the condition that the set of operators $T_L^M$ satisfy the commutation relations

$$[J_x \pm iJ_y,\, T_L^M ] = [(L \mp M)(L \pm M + 1)]^{1/2}\, T_L^{M \pm 1}$$

$$[J_z,\, T_L^M ] = M\, T_L^M  \qquad (10\text{-}12)$$

Both definitions may be shown to be equivalent. The second is the one given by Racah[8]. Since the proof is relatively simple we shall sketch it briefly.

We shall first remember the connection between the rotation operators and the angular momentum operators, Eq. (5-4),

$$R_n(\phi) = e^{i\phi (n \cdot J)} \tag{10-13}$$

$\phi$ is the angle of rotation about the axis defined by the unit vector $n$, and $(n \cdot J)$ is the component of the angular momentum along that axis. This expression is often taken as the definition of the angular momentum operators. One should also remember that the $D^L_{M'M}(\phi)$ are nothing else than the matrix elements of R in the basis afforded by the spherical harmonics $Y^M_L$.

$$D^L_{M'M} = (LM' \mid R \mid LM) = (LM' \mid e^{i\phi(n \cdot J)} \mid LM) \tag{10-14}$$

For an infinitesimal rotation we may expand $R$ in the form

$$R = e^{i\phi (n \cdot J)} = 1 + i\phi (n \cdot J) + \dots \tag{10-15}$$

Eq. (10-14) now takes the form

$$D^L_{M'M} = (LM' \mid 1 + i\phi (n \cdot J) \mid LM) \tag{10-16}$$

$$= \delta(M',M) + i\phi (LM' \mid (n \cdot J) \mid LM)$$

We can now substitute the above results in (10-11) keeping terms only up to the first order in $\phi$.

For the left hand side of (10-11) we obtain

$$R \, T^M_L \, R^{-1} = (1 + i\phi (n \cdot J)) \, T^M_L \, (1 - i\phi (n \cdot J)) \tag{10-17}$$

$$= T^M_L + i\phi ((n \cdot J) \, T^M_L - T^M_L (n \cdot J))$$

For the right hand side,

$$\sum_{M'} D^L_{M'M} \, T^{M'}_L = T^M_L + i\phi \sum_{M'} (LM' \mid (n \cdot J) \mid LM) \, T^{M'}_L \tag{10-18}$$

and finally

$$[(n \cdot J), T_L^M] = \sum_M T_L^{M'} (LM' | (n \cdot J) | LM) \tag{10-19}$$

We only have to substitute on the right hand side the values of the matrix elements of the components of the angular momentum. The non-vanishing elements are

$$(L, M+1 | J_x + iJ_x | LM) = [(L-M)(L+M+1)]^{1/2}$$

$$(L, M-1 | J_x - iJ_y | LM) = [(L+M)(L-M+1)]^{1/2} \tag{10-20}$$

$$(L M | J_z | LM) = M$$

Substitution in (10-19) gives the commutation relations (10-12).


## ADDITION AND MULTIPLICATION OF TENSORS

Two tensors of the same rank may be added to give another tensor of the same rank.

Also, two irreducible spherical tensors $T_{L_1}$ and $T_{L_2}$ may be "coupled" to give other irreducible tensors with ranks L such that $|L_1 - L_2| \leq L \leq L_1 + L_2$.

The addition and multiplication of tensors will be treated in some more detail in the next Section.

We consider now some general properties of tensor operators in the spherical basis. We assume that the basis functions $|jm)$ are eigenfunctions of (the total) $J^2$ and $J_z$ of the system.

In the commutation relation (10-12,b)

$$J_z T_L^M - T_L^M J_z = M\,T_L^M \tag{10-21}$$

we can multiply on the left by $(jm|$, and on the right by $|j'm')$. We obtain

$$m\,(jm|T_L^M\,|j'm') - m'(jm|\,T_L^M\,|j'm') = M\,(jm|\,T_L^M\,|j'm') \tag{10-22}$$

or

$$(m - m' - M)\,(jm|T_L^M\,|\,j'm') = 0,$$

so that the only non-vanishing elements will be those for which $m = M + m'$. Within a given $j, j'$ submatrix they are all along a parallel to the main diagonal $jm, jm$, just as in the case of the matrix elements of the spherical harmonics or $J_1, J_0, J_{-1}$.

If the same procedure is applied to the other commutation relations (10-12,a)

$$[J_x \pm iJ_y,\, T_L^M\,] = |\,(L \mp M)\,(L \pm M + 1)\,|^{1/2}\,T_L^{M\,\pm\,1} \tag{10-23}$$

one obtains *recurrence relations* between matrix elements with the same $L, j, j'$ and adjacent $M, m,$ and $m'$. These may be written as

$$f(L, M+1)\,(jm|T_L^M\,|\,j'm') = f(j, m+1)(j, m+1\,|\,T_L^{M+1}\,|j'm') - f(j', m')\,(jm\,|T_L^{M+1}|j'm'-1) \tag{10-24}$$

$$f(L, M)\,(jm|\,T_L^M\,|j'm') = f(j, m)\,(jm-1|\,T^{M-1}|j'm') - f(j', m+1)(jm|T_L^{M-1}|j'm'+1) \tag{10-25}$$

where

$$f(j,\,m) = \sqrt{(j+m)\,(j-m+1)} \tag{10-26}$$

It is important to notice that if one matrix element $(jm|T_L^M|j'm') \neq 0$ is known, all the elements for allowed values of m, m', and M and the same j, j', L, can be determined by means of the recursion relations. Also important is the fact that the Clebsch-Gordan coefficients $(j'm'LM|jm)$ satisfy the same recursion formulae (See (8-10,11) as the $(jm|T_L^M|j'm')$, and both vanish unless $M + m' = m$. From this, and the linear nature of the recursion relation follows the

*Wigner — Eckart Theorem.*

This states that the matrix elements $(jm|T_L^M|j'm')$ are proportional to the Clebsch-Gordan coefficients

$$(jm|T_L^M|j'm') = \frac{(j||T_L||j')}{(2j+1)^{1/2}} \; (j'm'LM|jm). \tag{10-27}$$

the ratio being independent of the projection quantum numbers m, m', and M. It is only determined by the physical properties of the tensor operator and the system. The geometrical properties, which depend on the orientation of the reference frame, are entirely contained in the Clebsch-Gordan coefficient.

$(j||T_L||j')$ is called the *reduced matrix element* of the tensor operator $T_L$. This is the factor that differentiates two tensors of the same rank.

As in the case of the Clebsch-Gordan coefficients, the "double-bar" matrix elements may be defined in several ways (See Edmonds,[2] p. 88). The definition given is equivalent to that of Edmonds and Racah, the only difference being one of notation

$$(ajm|T_L^M|a'j'm')$$

$$= (-1)^{j-m} (aj||T_L||a'j) \begin{pmatrix} j & L & j' \\ -m & M & m' \end{pmatrix} \tag{10-28}$$

$$= (-1)^{j+m} (aj||T_L||a'j') \cdot V(jj'L; -mm'M)$$

*Physical Interpretation of* $(aj||T_L||a'j')$

In virtue of the orthogonality of the Clebsch-Gordan coefficients it easily follows that

$$\sum_{m,M,m'} |(\alpha jm| T_L^M |\alpha'j'm')|^2 = |(\alpha j || T_L || \alpha'j')|^2 \qquad (10\text{-}29)$$

In radiation theory, if $T_L$ is the operator inducing transitions, the sum (10-29) over magnetic quantum numbers and polarizations is defined as the *line strength* of the transition (Condon and Shortley[9], p. 98)

$$S(\alpha j, \alpha'j') = |(\alpha j || T_L || \alpha'j')|^2 \qquad (10\text{-}30)$$

and is symmetrical in the initial and final states.

*The Reduced Matrix Elements of* J *and* $Y_L$

The $(j || T_L || j')$ are usually determined from (10-27, 28) after computing the easiest of the $(jm| T_L^M |j'm')$. For the *angular momentum operator* one obtains

$$(j || J || j') = [j(j+1)(2j+1)]^{\frac{1}{2}} \delta(j, j') \qquad (10\text{-}31)$$

For the *spherical harmonics*, we have

$$(\ell || Y_L || \ell') = (-1)^{\ell} \left[ \frac{(2\ell+1)(2L+1)(2\ell'+1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

$$= (-1)^{g-\ell} \left[ \frac{(2\ell+1)(2L+1)(2\ell'+1)}{4\pi(\ell+L+\ell'+1)} \right]^{\frac{1}{2}} \frac{\begin{pmatrix} g \\ \ell \end{pmatrix} \begin{pmatrix} \ell \\ g-\ell' \end{pmatrix}}{\left[ \begin{pmatrix} 2g \\ 2\ell \end{pmatrix} \begin{pmatrix} 2\ell \\ 2g-2\ell \end{pmatrix} \right]^{\frac{1}{2}}} \qquad (10\text{-}32)$$

where $g = (\ell + L + \ell')/2$ must be an integer.

# 11. IRREDUCIBLE TENSOR OPERATORS

The concepts and results of the previous section may be easily generalized to groups of symmetry other than spherical. We shall consider groups of unitary operators and, as usual, we will assume that the matrices of the irreducible representations are chosen to be unitary.*

Consider a set of operators $T_\mu^{(\gamma)}$, where $\mu$ assumes $d_\gamma$ different values, which under the operations R of the group transform always into linear combinations of themselves, in the form given by Eq. (3-7)

$$R \, T_\mu^{(\gamma)} \, R^{-1} = \sum_\lambda T_\lambda^{(\gamma)} \, (\gamma\lambda|R|\gamma\mu) \tag{11-1}$$

The matrices with elements $(\gamma\lambda|R|\gamma\mu)$ afford a representation of the group. If this representation is irreducible, the set of $d_\gamma$ operators is said to constitute an irreducible tensor operator $T^{(\gamma)}$ belonging to the irreducible representation $\Gamma$ of the group. The individual operators $T_\mu^{(\gamma)}$ are designated as the components of $T^{(\gamma)}$, and in particular $T_\lambda^{(\gamma)}$ is said to belong to the $\lambda$-th row of the representation. As in the case of the basis functions, this definition is made in reference to a particular matrix representation. In what follows, we shall assume that the tensor components $T_\mu^{(\gamma)}$ and the basis functions $|\gamma\mu)$ transform under the group operations by the same representation matrices, so that

$$R|\alpha\gamma\mu) = \Sigma \, |\alpha\gamma\lambda) \, (\gamma\lambda|R|\gamma\mu) \tag{11-2}$$

In virtue of the analogy between Eqs. (11-1) and (11-2), the algebra of tensor operators may be developed along similar lines to that of the basis functions.

---

* In Section 10, irreducible spherical tensors have been introduced by way of the operators corresponding to the spherical harmonics $Y_L^M$, and the notation $T_L^M$ was used to preserve the analogy. From now on we shall follow the most prevalent notation in the literature of tensor operators. In this notation the previous $T_L^M$ will be written as $T_M^{(L)}$.

By analogy with the definitions of "projection operators" we may now define "projection transformations" or "step transformations", which act on the components of tensor operators in a corresponding fashion. By multiplying both sides of Eq. (11-1) by $(\gamma \lambda' |R| \gamma' \mu')^* d_{\gamma'}/h$ and adding over all the group operations, we obtain

$$\frac{d_{\gamma'}}{h} \sum_R (\gamma \lambda' |R| \gamma' \mu')^* R \, T_\mu^{(\gamma)} \, R^{-1}$$

$$= \sum_\lambda T_\lambda^{(\gamma)} \frac{d_{\gamma'}}{h} \sum_R (\gamma \lambda' |R| \gamma' \mu')^* (\gamma \lambda |R| \gamma \mu)$$

$$= \sum_\lambda T_\lambda^{(\gamma)} \, \delta(\lambda', \lambda) \, \delta(\gamma', \gamma) \, \delta(\mu', \mu)$$

$$= \delta(\gamma', \gamma) \, \delta(\mu', \mu) \, T_\lambda^{(\gamma')}$$

(11-3)

where we have made use of the orthogonality relations, Eq. (3-13).

The transformation analog of the expression (4-14) for the projection operators may be written symbolically as

$$O_{\lambda\mu}^{(\gamma)} = \frac{d_\gamma}{h} \sum_R (\gamma \lambda |R| \gamma \mu)^* \, R| \quad |R^{-1}$$

(11-4)

where the operator expression $R| \quad |R^{-1}$ on the right-hand side has been written in that form to indicate that it acts on an operator $T$ by means of a similarity transformation $RTR^{-1}$.

The analogs of Eqs. (4-9) and (4-10) are

$$O_{\lambda\mu}^{(\gamma)} \, T_\mu^{(\gamma')} = T_\lambda^{(\gamma)} \, \delta(\gamma, \gamma') \, \delta(\mu, \mu')$$

(11-5)

$$O_{\lambda\mu}^{(\gamma)} \, O_{\mu'\nu}^{(\gamma')} = O_{\lambda\nu}^{(\gamma)} \, \delta(\gamma, \gamma') \, \delta(\mu, \mu')$$

(11-6)

The $O_{\lambda\mu}^{(\gamma)}$ will be designated as "projection transformations" or "step transformations".

The decomposition of reducible operators into irreducible tensor operators follows along the same lines as for basis functions.

## THE ADJOINT OF A TENSOR OPERATOR

The transformation properties of the adjoint of a tensor operator $T^{(\gamma)}$ may be obtained from Eq. (11-1). Since the R are unitary, we obtain

$$R \, T^{(\gamma) \, \dagger}_{\mu} \, R^{-1} = \sum_{\lambda} \, T^{(\gamma) \, \dagger}_{\lambda} \, (\gamma\lambda \, |R| \gamma\mu)^* \tag{11-7}$$

and therefore $T^{(\gamma) \, \dagger}$ belongs to the complex conjugate representation $\Gamma^*$.

For the most important groups that we shall consider, the representations afforded by the matrices $D(R)$ and $D(R)^*$ are equivalent

$$C \, D(R) \, C^{-1} = D(R)^* \tag{11-8}$$

and $T^{(\gamma)}$ is self-adjoint. The relation between the components of $T^{(\gamma)}$ and $T^{(\gamma) \, \dagger}$ is, according to Eqs. (3-3) and (3-5)

$$T^{(\gamma)}_{\mu} = \sum_{\mu'} \, T^{(\gamma) \, \dagger}_{\mu'} \, (\gamma\mu' \, | C | \gamma\mu) \tag{11-9}$$

In spherical basis, the matrix elements of $C$ may be taken as (Ref. 1, p. 288)

$$(JM' \, |C| \, JM) = (-1)^{J-M} \, \delta(M', -M) \tag{11-10}$$

apart from a common arbitrary phase factor, and therefore

$$T^{(J)}_{M} = (-1)^{J-M} \, T^{(J) \, \dagger}_{-M}$$

$$T^{(J) \, \dagger}_{M} = (-1)^{J+M} \, T^{(J)}_{-M} \tag{11-11}$$

However, the definition introduced by Racah[8], which is the one most widely followed in the literature, is instead

$$T^{(K) \, \dagger}_{Q} = (-1)^{Q} \, T^{(K)}_{-Q} \tag{11-12}$$

which follows the conventions in the usual definition of the spherical harmonics (Cf. Eq. 10-10). We also follow this definition in the present work when dealing with sperical tensors.

11-3

Two tensor operators transforming under the operations of the group according to the same representation matrices may be added to give another tensor operator with the same transformation properties. This follows from the linear nature of Eq. (11-1).

As in the case of the basis functions, two irreducible tensor operators $T^{(\gamma_1)}$ and $T^{(\gamma_2)}$ may be coupled to give tensor operators $T^{(\gamma)}$ belonging to the different irreducible representations contained in the direct product $\Gamma_1 \times \Gamma_2$. The coupling expressions are analogous to Eqs. (8-40) and (8-41)

$$T^{(\alpha\gamma)}_\mu = \sum_{\mu_1,\mu_2} T^{(\gamma_1)}_{\mu_1} T^{(\gamma_2)}_{\mu_2} (\gamma_1\mu_1\gamma_2\mu_2|\alpha\gamma\mu) \tag{11-13}$$

$$T^{(\gamma_1)}_{\mu_1} T^{(\gamma_2)}_{\mu_2} = \sum_{\alpha\gamma\mu} T^{(\alpha\gamma)}_\mu (\alpha\gamma\mu|\gamma_1\mu_1\gamma_2\mu_2) \tag{11-14}$$

where the coupling coefficients are the same as for the basis functions. This is easily proved, since by use of Eq. (11-5) the derivation given in Section 8, Eqs. (8-45) to (8-52) may be reproduced with the projection transformation $O^{(\gamma)}_{\mu'\mu}$ acting on the operator product $T^{(\gamma_1)}_{\mu_1} T^{(\gamma_2)}_{\mu_2}$.

The coupling of two tensor operators $S^{(\gamma)}$ and $T^{(\gamma)\,\dagger}$ which transform according to complex conjugate representations gives, besides others, a tensor which is invariant under the operations of the group. The coupling coefficients for this case may be obtained very easily from Eq. (8-48) taking into account the orthogonality relations for the $(\gamma\mu'|R|\gamma\mu)$ and the fact that for the identical representation A, the matrix elements are

$$(A0|R|A0) = 1 \tag{11-15}$$

For the non-vanishing coupling coefficients Eq. (8-48) gives

$$(\gamma\mu\bar{\gamma}\mu|A0)(\gamma\mu'\bar{\gamma}\mu'|A0)^* = \frac{1}{d_\gamma} \tag{11-16}$$

where the labels $\gamma$ and $\bar{\gamma}$ are used for complex conjugate representations. We can write

$$(\gamma\mu\,\bar{\gamma}\mu|A0) = e^{i\phi}/\sqrt{d_\gamma} \tag{11-17}$$

where $e^{i\phi}$ is an arbitrary phase factor.

The coupling expression for the invariant $I^{(A)}$ is therefore, setting $e^{i\phi} = 1$,

$$I_0^{(A)} = \frac{1}{\sqrt{d_\gamma}} \sum_\mu S_\mu^{(\gamma)} T_\mu^{(\gamma)\,\dagger} \tag{11-18}$$

In spherical basis, every representation is equivalent to its complex conjugate. The equivalent of the previous equations is

$$I_0^{(0)} = \frac{1}{\sqrt{2J+1}} \sum_M (-1)^{J-M} S_M^{(J)} T_{-M}^{(J)} \tag{11-19}$$

However, the scalar product of two tensor operators is usually defined as

$$S^{(J)} \cdot T^{(J)} = \sum_M (-1)^M S_M^{(J)} T_{-M}^{(J)} \tag{11-20}$$

which differs from the previous $I_0^{(0)}$ by a factor of $(-1)^J / \sqrt{2J+1}$.

## GENERAL FORMULATION OF THE WIGNER-ECKART THEOREM

We shall now consider the factorization of the matrix elements of the components of tensor operators between basis functions classified according to the irreducible representations of the group.

By means of Eqs. (11-1) and (11-2) a typical matrix element may be expressed as follows

$$(a_3 \gamma_3 \mu_3 \mid T_\mu^{(\gamma)} \mid a_1 \gamma_1 \mu_1) = (a_3 \gamma_3 \mu_3 \mid R^{-1} R \, T_\mu^{(\gamma)} R^{-1} R \mid a_1 \gamma_1 \mu_1)$$

$$= (R a_3 \gamma_3 \mu_3 \mid R \, T_\mu^{(\gamma)} R^{-1} \mid R a_1 \gamma_1 \mu_1)$$

$$= \sum_{\lambda_1, \lambda, \lambda_3} (a_3 \gamma_3 \lambda_3 \mid T_\lambda^{(\gamma)} \mid a_1 \gamma_1 \lambda_1)(\gamma_1 \lambda_1 \mid R \mid \gamma_1 \mu_1)(\gamma \lambda \mid R \mid \gamma \mu)(\gamma_3 \lambda_3 \mid R \mid \gamma_3 \mu_3)^*$$

$$\tag{11-21}$$

Adding over all the group operations and dividing by $h$ we get

$$(a_3 \gamma_3 \mu_3 | T_\mu^{(\gamma)} | a_1 \gamma_1 \mu_1) =$$

$$= \frac{1}{h} \sum_{\lambda_1, \lambda, \lambda_3} (a_3 \gamma_3 \lambda_3 | T_\lambda^{(\gamma)} | a_1 \gamma_1 \lambda_1) \sum_R (\gamma_1 \lambda_1 | R | \gamma_1 \mu_1)(\gamma \lambda | R | \gamma \mu)(\gamma_3 \lambda_3 | R | \gamma_3 \mu_3)^*$$

$$(11\text{-}22)$$

The sum over R on the right-hand side may be expressed in terms of products of coupling coefficients by means of Eqs. (8-48) or (8-52). If the irreducible representation $\Gamma_3$, of dimension $d_3$, is contained $n_3$ times in the product $\Gamma_1 \times \Gamma$, we have

$$(a_3 \gamma_3 \mu_3 | T_\mu^{(\gamma)} | a_1 \gamma_1 \mu_1) =$$

$$\sum_{\lambda_1, \lambda, \lambda_3} (a_3 \gamma_3 \lambda_3 | T_\lambda^{(\gamma)} | a_1 \gamma_1 \lambda_1) \sum_\beta^{n_3} \frac{1}{d_3} (\gamma_1 \lambda_1 \gamma \lambda | \beta \gamma_3 \lambda_3)(\gamma_1 \mu_1 \gamma \mu | \beta \gamma_3 \mu_3)^*$$

$$= \sum_\beta^{n_3} \frac{1}{\sqrt{d_3}} (\gamma_1 \mu_1 \gamma \mu | \beta \gamma_3 \mu_3)^* \sum_{\lambda_1, \lambda, \lambda_3} \frac{1}{\sqrt{d_3}} (\gamma_1 \lambda_1 \gamma \lambda | \beta \gamma_3 \lambda_3)(a_3 \gamma_3 \lambda_3 | T_\lambda^{(\gamma)} | a_1 \gamma_1 \lambda_1)$$

$$(11\text{-}23)$$

The summations over $\lambda_1$, $\lambda$, and $\lambda_3$ on the right-hand side are obviously independent of the indices labelling the rows of the representations. We shall write them in the form

$$(a_3 \gamma_3 || T^{(\beta \gamma)} || a_1 \gamma_1) =$$

$$\sum_{\lambda_1, \lambda, \lambda_3} \frac{1}{\sqrt{d_3}} (\gamma_1 \lambda_1 \gamma \lambda | \beta \gamma_3 \lambda_3)(a_3 \gamma_3 \lambda_3 | T_\lambda^{(\gamma)} | a_1 \gamma_1 \lambda_1)$$

$$(11\text{-}24)$$

and they are usually designated as the "reduced matrix elements". With this definition Eq. (11-23) may now be written

$$(a_3 \gamma_3 \mu_3 | T_\mu^{(\gamma)} | a_1 \gamma_1 \mu_1) = \sum_\beta^{n_3} \frac{1}{\sqrt{d_3}} (\gamma_1 \mu_1 \gamma \mu | \beta \gamma_3 \mu_3)^* (a_3 \gamma_3 || T^{(\beta \gamma)} || a_1 \gamma_1)$$

$$= \sum_\beta^{n_3} \frac{1}{\sqrt{d_3}} (\beta \gamma_3 \mu_3 | \gamma_1 \mu_1 \gamma \mu)(a_3 \gamma_3 || T^{(\beta \gamma)} || a_1 \gamma_1) \qquad (11\text{-}25)$$

If the product $\Gamma_1 \times \Gamma$ contains the representation $\Gamma_3$ only once the expression of the Wigner-Eckart theorem takes the simpler form

$$(\alpha_3\gamma_3\mu_3 | T_\mu^{(\gamma)} | \alpha_1\gamma_1\mu_1) =$$

$$= \frac{1}{\sqrt{d_3}} \ (\gamma_1\mu_1\gamma\mu | \gamma_3\mu_3)^* \ (\alpha_3\gamma_3 || T^{(\gamma)} || \alpha_1\gamma_1)$$

$$= \frac{1}{\sqrt{d_3}} \ (\gamma_3\mu_3 | \gamma_1\mu_1\gamma\mu) \ (\alpha_3\gamma_3 || T^{(\gamma)} || \alpha_1\gamma_1) \qquad (11\text{-}26)$$

Similarly the expression for the reduced matrix elements, Eq. (11-24) also takes a simpler form, where the index $\beta$ does not appear. It may be mentioned that the summation over one of the indices may be replaced by multiplication by the dimension of the corresponding representation.

It may be worthwhile pointing out that Eq. (11-25) can always be cast into the form of Eq. (11-26), but this amounts essentially to a new definition of the coupling coefficients by the condition that the reduced matrix elements of the tensor operator in question should vanish for all but one value of the index $\beta$.

The Wigner-Eckart theorem forms the basis for the symmetry selection rules. The theorem concerning the matrix elements of symmetric operators, Eq. (3-19), is also a particular case.

The corresponding rule for non totally symmetric operators may now be enunciated as follows: The matrix elements of the type $(\alpha_3\gamma_3\mu_3 | T_\mu^{(\gamma)} | \alpha_1\gamma_1\mu_1)$ vanish if the corresponding coupling coefficients $(\gamma_1\mu_1\gamma\mu | \gamma_3\mu_3)$ are zero. In addition, if the representation product $\Gamma_1 \times \Gamma$ does not contain the $\Gamma_3$ representation, these matrix elements vanish for all values of $\mu$, $\mu_1$, and $\mu_3$.

It should be kept in mind that this is only a sufficient, but not necessary condition, since the matrix elements may vanish because the reduced matrix element is zero. Thus, for example, the matrix elements of the spherical harmonics $(\ell m | Y_M^{(L)} | \ell'm')$ vanish for $\ell + L + \ell'$ odd, although the coupling coefficients for the corresponding representations of $R_3$ are not zero, in general. In this example the reason for the vanishing of the reduced matrix elements in question may be traced to still another symmetry requirement, namely the parity selection rules, which are obtained from the consideration of the inversion symmetry of the basis functions and operators.

As in previous instances, it is convenient to point out the differences with other definitions in the literature, which are not always equivalent. Our definition of tensor operators, Eq. (11-1) agrees with those followed by Rose[3], Edmonds[2], and Racah[8]. However, Wigner's original definition (Ref. 1, p. 244, Eq. 21.16c) is not equivalent to Eq. (11-1), but is rather

$$R \, T_\mu^{(\gamma)} \, R^{-1} = \sum_\lambda T_\lambda^{(\gamma)} \, (\gamma\lambda|R|\gamma\mu)^* \qquad (11\text{-}27)$$

and therefore the $T_\mu^{(\gamma)}$ tensor components are the adjoints of those defined by Eq. (11-1).

Ironically enough, our expression the the Wigner-Eckart theorem is not therefore equivalent to Wigner's since this leads to the following

$$(\alpha_3\gamma_3\mu_3| T_\mu^{(\gamma)} |\alpha_1\gamma_1\mu_1) = \frac{1}{\sqrt{d_1}} \, (\gamma_3\mu_3\gamma\mu|\gamma_1\mu_1) \, (\alpha_3\gamma_3|| \, T^{(\gamma)} \, ||\alpha_1\gamma_1) \qquad (11\text{-}28)$$

instead of Eq. (11-26).

For the general case, the definition adopted by Koster[7] is effectively the same as Eq. (11-1). In Ref. 7, the equation (4) defining the transformation of the tensor components appears to be incorrect, but in the subsequent derivation it is actually the equivalent of Eq. (11-1) that is used. The final expression is also equivalent to Eq. (11-25) although the resemblance is obscured by the introduction of the conjugate representations $\Gamma_3^*$ and $\Gamma^*$.

# 12. 6-J COEFFICIENTS AND REDUCED MATRIX ELEMENTS IN COUPLED SCHEMES

*THE COUPLING OF THREE ANGULAR MOMENTA*

The coupling of three angular momenta $j_1$, $j_2$, and $j_3$, to give states with definite total angular momentum $J$ may be carried out in essentially two different ways. One may first couple $j_1$ and $j_2$ to obtain states characterized by an "intermediate" $j_{12}$, and then couple these to $j_3$ to give final states with definite total $J$. Alternatively, one may couple $j_1$ to the intermediate $j_{23}$ states obtained by coupling $j_2$ and $j_3$.

The expression for the resultant states for a given value of $J$ is in the first case

$$|(j_1 j_2) j_{12}, j_3, J M) = \sum_{m_3} |j_{12} m_{12}) |j_3 m_3) (j_{12} m_{12} j_3 m_3 | J M) =$$

$$\sum_{m_1 m_3} |j_1 m_1) |j_2 m_2) |j_3 m_3) (j_1 m_1 j_2 m_2 | j_{12} m_{12}) (j_{12} m_{12} j_3 m_3 | J M) \qquad (12\text{-}1)$$

The $|J M)$ functions obtained in the second case are

$$|j_1, (j_2 j_3) j_{23}, J M) = \sum_{m_1} |j_1 m_1) |j_{23} m_{23}) (j_1 m_1 j_{23} m_{23} | J M) =$$

$$\sum_{m_1 m_3} |j_1 m_1) |j_2 m_2) |j_3 m_3) (j_2 m_2 j_3 m_3 | j_{23} m_{23}) (j_1 m_1 j_{23} m_{23} | J M) \qquad (12\text{-}2)$$

The two sets of $|J M)$ functions for a given value of $J$ obtained according to these two schemes are not identical, but are linearly related to one another. They constitute two equivalent representations which are related by a unitary transformation.

$$|j_1, (j_2 j_3) j_{23}, J M) = \sum_{j_{12}} |(j_1 j_2) j_{12}, j_3, J M) ((j_1 j_2) j_{12}, j_3, J | j_1, (j_2 j_3) j_{23}, J) \qquad (12\text{-}3)$$

The expression for the transformation coefficients is obtained by taking the Hermitian scalar product of the functions in Eqs. (12-1) and (12-2)

$$((j_1 j_2) j_{12}, j_3, J | j_1, (j_2 j_3) j_{23}, J) =$$

$$\sum_{m_1 m_3} (J M | j_{12} m_{12} j_3 m_3) (j_{12} m_{12} | j_1 m_1 j_2 m_2) \times (j_2 m_2 j_3 m_3 | j_{23} m_{23}) (j_1 m_1 j_{23} m_{23} | J M) \qquad (12\text{-}4)$$

A more convenient and symmetrical form of these transformation coefficients is afforded by Wigner's 6-j coefficients, defined by

$$
\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix} = \frac{(-1)^{j_1+j_2+j_3+J}}{\sqrt{(2j_{12}+1)\,(2j_{23}+1)}} ((j_1 j_2) j_{12}, j_3, J \mid j_1, (j_2 j_3) j_{23}, J) \tag{12-5}
$$

The 6-j symbol is invariant against any interchange of columns or the interchange of the upper and lower indices of any two columns. For example

$$
\begin{Bmatrix} j_1 & j_2 & j_3 \\ k_1 & k_2 & k_3 \end{Bmatrix} = \begin{Bmatrix} j_3 & j_2 & j_1 \\ k_3 & k_2 & k_1 \end{Bmatrix} = \begin{Bmatrix} j_1 & k_2 & k_3 \\ k_1 & j_2 & j_3 \end{Bmatrix} \tag{12-6}
$$

These and other symmetry relations will be consider in more detail in the Appendix dealing with symmetrized coupling coefficients.

The general expression for the 6-j symbol has been given by Racah[8]. It may be written in the form

$$
\begin{Bmatrix} j_1 & j_2 & j_3 \\ k_1 & k_2 & k_3 \end{Bmatrix} = \left[ \frac{(j_1 j_2 j_3)}{(j_1 k_2 k_3)\,(k_1 j_2 k_3)\,(k_1 k_2 j_3)} \right]^{\frac{1}{2}}
$$

$$
\times \sum_z (-1)^z \begin{pmatrix} z+1 \\ j_1+j_2+j_3+1 \end{pmatrix} \begin{pmatrix} j_1+j_2-j_3 \\ j_1+j_2+k_1+k_2-z \end{pmatrix} \begin{pmatrix} j_1-j_2+j_3 \\ j_1+j_3+k_1+k_3-z \end{pmatrix} \begin{pmatrix} -j_1+j_2+j_3 \\ j_2+j_3+k_2+k_3-z \end{pmatrix} \tag{12-7}
$$

where the factors in the summation are binomial coefficients, while the symbols (a b c) are given by

$$
(a\,b\,c) = \frac{(a+b+c+1)!}{(-a+b+c)!\,(a-b+c)!\,(a+b-c)!} \tag{12-8}
$$

and are thus closely related to the trinomial coefficients. The index $z$ runs over all the

positive integral values such that $n \geqslant r \geqslant 0$ for every binominal coefficient $\binom{n}{r}$ in the sum.

The 6-j coefficients vanish for those sets of values of the arguments for which any of the (a b c) does not satisfy the triangular condition.

The 6-j coefficients play an important role in the expressions relating reduced matrix elements of spherical tensor operators in different coupling schemes.

The numerical values of 6-j symbols required in our work have been obtained by means of a program for the IBM electronic computer, to which we make reference in the Tables.

## REDUCED MATRIX ELEMENTS IN COUPLED SCHEMES

In practical applications, it is often necessary to determine the matrix elements of operators which are obtained from others by the coupling schemes previously discussed. Similarly, it is also often convenient to choose a system of basis functions resulting from the coupling of functions of other bases.

In this respect, there are a number of important results relating the reduced matrix elements in the different schemes.

*COUPLED TENSORS IN COMMON BASIS*

Let us consider two irreducible spherical tensors $T^{(k_1)}$ and $T^{(k_2)}$ which operate on the same set of basis functions. We shall derive an expression for the reduced matrix elements of the coupled tensor $T^{(k)}$

$$T_q^{(k)} = \sum_{q_1} T_{q_1}^{(k_1)} T_{q_2}^{(k_2)} (k_1 q_1 k_2 q_2 | k q) \tag{12-9}$$

in the same set of basis functions in terms of the reduced matrix elements of the individual tensor operators.

The reduced matrix elements of $T^{(k)}$ are given by

$$(\alpha j \| T^{(k)} \| \alpha' j') = \sqrt{2j+1} \sum_m (\alpha j m | T_q^{(k)} | \alpha' j' m')(j' m' k q | j m) \tag{12-10}$$

which is a particular case of Eq. (11-24) after the sum over $m$ is carried out.

The matrix elements appearing on the right-hand side may be expressed in terms of those for $T^{(k_1)}$ and $T^{(k_2)}$ by means of Eq. (12-9)

$$(a j m | T_q^{(k)} | a' j' m') = \sum_{q_1} (k_1 q_1 k_2 q_2 | k q) (a j m | T_{q_1}^{(k_1)} T_{q_2}^{(k_2)} | a' j' m') =$$

$$\sum_{q_1} (k_1 q_1 k_2 q_2 | k q) \sum_{a'' j'' m''} (a j m | T_{q_1}^{(k_1)} | a'' j'' m'') (a'' j'' m'' | T_{q_2}^{(k_2)} | a' j' m') \qquad (12\text{-}11)$$

The reduced matrix elements of $T^{(k_1)}$ and $T^{(k_2)}$ may now be introduced by use of the Wigner-Eckart theorem

$$(a j m | T_q^{(k)} | a' j' m') = \sum_{a'' j''} (a j \| T^{(k_1)} \| a'' j'') (a'' j'' \| T^{(k_2)} \| a' j') \times$$

$$\sum_{q_1 m''} \frac{1}{\sqrt{(2j+1)(2j''+1)}} (k_1 q_1 k_2 q_2 | k q) (j'' m'' k_1 q_1 | j m) (j' m' k_2 q_2 | j'' m'') \quad (12\text{-}2)$$

When this is introduced in Eq. (12-10) a summation over products of four coupling coefficients appears on the right-hand side, which may be expressed in terms of a 6-j coefficient

$$\frac{1}{\sqrt{2j''+1}} \sum_{m' m'' q_1} (j' m' k q | j m)(k_1 q_1 k_2 q_2 | k q)(j'' m'' k_1 q_1 | j m)(j' m' k_2 q_2 | j'' m'') =$$

$$(-1)^{j+k+j'} \sqrt{2k+1} \begin{Bmatrix} j & k & j' \\ k_2 & j'' & k_1 \end{Bmatrix} \qquad (12\text{-}13)$$

The final expression relating the reduced matrix elements of $T^{(k)}$ to those of $T^{(k_1)}$ and $T^{(k_2)}$ is

$$(a j \| T^{(k)} \| a' j') =$$

$$(-1)^{j+k+j'} \sqrt{2k+1} \sum_{a'' j''} (a j \| T^{(k_1)} \| a'' j'')(a'' j'' \| T^{(k_2)} \| a' j') \begin{Bmatrix} j & k & j' \\ k_2 & j'' & k_1 \end{Bmatrix}$$

$$(12\text{-}14)$$

It is also of interest to derive expressions for the reduced matrix elements of tensors $S^{(k_1)}$ and $T^{(k_2)}$ which operate on different sets of basis functions $|\alpha_1 j_1 m_1\rangle$ and $|\alpha_2 j_2 m_2\rangle$, respectively, in a basis $|\alpha J M\rangle$ obtained by coupling basis functions of both sets, in terms of the reduced matrix elements of $S^{(k_1)}$ and $T^{(k_2)}$ in their respective bases.

The simplest case to consider is that of an operator which acts only on the functions $|\alpha_1 j_1 m\rangle$ or $|\alpha_2 j_2 m_2\rangle$. We shall omit the derivations at this point, and just quote the results.

$$(\alpha j_1 j_2, J \| S^{(k_1)} \| \alpha' j_1' j_2', J') =$$

$$(-1)^{j_1+j_2+J'+k_1} \sqrt{(2J+1)(2J'+1)}\ (\alpha j_1 \| S^{(k_1)} \| \alpha' j_1')\ \delta(j_2,j_2') \begin{Bmatrix} J & k_1 & J' \\ j_1' & j_2 & j_1 \end{Bmatrix} \quad (12\text{-}15)$$

Similarly, for $T^{(k_2)}$

$$(\alpha j_1 j_2, J \| T^{(k_2)} \| \alpha' j_1' j_2', J') =$$

$$(-1)^{j_1'+j_2'+J^*+k_2} \sqrt{(2J+1)(2J'+1)}\ (\alpha j_2 \| T^{(k_2)} \| \alpha' j_2')\ \delta(j_1,j_1') \begin{Bmatrix} J & k_2 & J' \\ j_2' & j_1 & j_2 \end{Bmatrix} \quad (12\text{-}16)$$

Another important case is that of the scalar product of two such tensors. We shall write $k = k_1 = k_2$.

$$(\alpha j_1 j_2, J \| S^{(k)} \cdot T^{(k)} \| \alpha' j_1' j_2', J') =$$

$$(-1)^{j_1'+j_2+J} \sqrt{2J+1}\ \delta(J,J') \begin{Bmatrix} j_1 & k & j_1' \\ j_2' & J & j_2 \end{Bmatrix} \sum_{\alpha''} (\alpha j_1 \| S^{(k)} \| \alpha'' j_1')(\alpha'' j_2 \| T^{(k)} \| \alpha' j_2')$$

$$(12\text{-}17)$$

The general case of the tensor product $X^{(K)}$ of $S^{(k_1)}$ and $T^{(k_2)}$ involves the 9-j symbols

$$(\alpha j_1 j_2 J \| X^{(K)} \| \alpha' j_1' j_2' J') = \sqrt{(2J + 1)(2K + 1)(2J' + 1)}$$

$$\times \sum_{\alpha''} (\alpha j_1 \| S^{(k_1)} \| \alpha'' j_1')(\alpha'' j_2 \| T^{(k_2)} \| \alpha' j_2') \begin{Bmatrix} j_1 & k_1 & j_1' \\ J & K & J' \\ j_2 & k_2 & j_2' \end{Bmatrix} \qquad (12\text{-}18)$$

The 9-j symbols are related to the transformation coefficients between two coupling schemes of four angular momentum vectors

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = \frac{((j_1 j_2) j_{12}, (j_3 j_4) j_{34}, j \mid (j_1 j_3) j_{13}, (j_2 j_4) j_{24}, j)}{\sqrt{(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)}} \qquad (12\text{-}19)$$

They may be expressed as a summation over products of six 3-j coefficients, and also as a summation over products of three 6-j coefficients[2], in the form

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} = \sum_{\lambda} (-1)^{2\lambda}(2\lambda + 1) \begin{Bmatrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & \lambda \end{Bmatrix} \begin{Bmatrix} j_{12} & j_{22} & j_{32} \\ j_{21} & \lambda & j_{23} \end{Bmatrix} \begin{Bmatrix} j_{13} & j_{23} & j_{33} \\ \lambda & j_{11} & j_{12} \end{Bmatrix}$$

$$(12\text{-}20)$$

# 13. UNIT TENSOR OPERATORS IN SPHERICAL BASIS

From the Wigner-Eckart theorem it follows that operators may be defined by specifying the values of their reduced matrix elements. This is a convenient form of definition for many different types of operators such as raising, lowering, coupling, etc.

Of particular interest are the unit tensor operators $u^{(k)}$ of Racah[8], which play an important role in the treatment of the several-electron problem. In a later Section we shall consider their relation to the infinitesimal operators of the rotation groups in several dimensions. At present we shall consider the one-electron case and show how the $u_q^k$ can be related to the familiar angular momentum operators and to the coordinate operators in spherical basis.

The unit tensor operators $u^{(k)}$ are defined by the condition that their reduced matrix elements are unity between states with the same $aj$, and zero otherwise

$$(a'j' \| u^{(k)} \| aj) = \delta(j',j)\,\delta(a',a) \tag{13-1}$$

Their matrix elements are therefore (omitting the index $a$)

$$(jm'|u_q^{(k)}|jm) = (2j+1)^{-\frac{1}{2}}(jm\,kq|jm') = (-1)^{j-m'}\begin{pmatrix} j & k & j \\ -m' & q & m \end{pmatrix} \tag{13-2}$$

In virtue of the Wigner-Eckart theorem, the matrix elements of a tensor operator $\mathbf{T}^{(k)}$ in spherical basis between the same states are proportional to those of $u^{(k)}$, the constant of proportionality being the reduced matrix element of $\mathbf{T}^{(k)}$

$$(jm'|T_q^{(k)}|jm) = (j \| \mathbf{T}^{(k)} \| j)(jm'|u_q^{(k)}|jm) \tag{13-3}$$

For a given basis, characterized by a certain value of $\underline{j}$, the operators $u_q^{(k)}$ for $k > 2j$ are identically zero, since the corresponding coupling coefficients vanish.

According to Eq. (13-2) the non-vanishing matrix elements of $u_q^{(k)}$ are along the q-th parallel to the main diagonal. Moreover, for a given value of $\underline{q}$, the matrix elements of operators with different $\underline{k}$ values satisfy the following orthogonality relations

$$\sum_m (j,\,m+q|u_q^{(k)}|jm)(j,\,m+q|u_q^{(k')}|jm) = \frac{\delta(k,k')}{2k+1} \tag{13-4}$$

In order to illustrate these facts, we reproduce in Table 13-1 the matrices for the non-vanishing $u_q^{(k)}$ operators in the space of the basis functions for $j = 1$.

TABLE 13-1

$$u_0^{(0)}$$

$$\sqrt{\frac{1}{3}}\begin{vmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{vmatrix}$$

$$\sqrt{3}\,u_1^{(1)} \qquad\qquad \sqrt{3}\,u_0^{(1)} \qquad\qquad \sqrt{3}\,u_{-1}^{(1)}$$

$$\sqrt{\frac{1}{2}}\begin{vmatrix}0 & -1 & 0\\0 & 0 & -1\\0 & 0 & 0\end{vmatrix} \qquad \sqrt{\frac{1}{2}}\begin{vmatrix}1 & 0 & 0\\0 & 0 & 0\\0 & 0 & -1\end{vmatrix} \qquad \sqrt{\frac{1}{2}}\begin{vmatrix}0 & 0 & 0\\1 & 0 & 0\\0 & 1 & 0\end{vmatrix}$$

$$\sqrt{5}\,u_2^{(2)} \quad\quad \sqrt{5}\,u_1^{(2)} \quad\quad \sqrt{5}\,u_0^{(2)} \quad\quad \sqrt{5}\,u_{-1}^{(2)} \quad\quad \sqrt{5}\,u_{-2}^{(2)}$$

$$\begin{vmatrix}0 & 0 & 1\\0 & 0 & 0\\0 & 0 & 0\end{vmatrix} \; \sqrt{\frac{1}{2}}\begin{vmatrix}0 & -1 & 0\\0 & 0 & 1\\0 & 0 & 0\end{vmatrix} \; \sqrt{\frac{1}{6}}\begin{vmatrix}1 & 0 & 0\\0 & -2 & 0\\0 & 0 & 1\end{vmatrix} \; \sqrt{\frac{1}{2}}\begin{vmatrix}0 & 0 & 0\\1 & 0 & 0\\0 & -1 & 0\end{vmatrix} \; \begin{vmatrix}0 & 0 & 0\\0 & 0 & 0\\1 & 0 & 0\end{vmatrix}$$

Any $(3 \times 3)$ matrix may be expressed as a linear combination of these nine matrices. It may also be noticed that the $|jm)$ for $j = 1$ are eigenfunctions of $u_0^{(0)}$, $u_0^{(1)}$, and $u_0^{(2)}$, which are therefore a complete set of commuting operators in that particular space.

The matrix elements of $u^{(k)}$ for a given $q$ may be considered as the components of a vector in $2j + 1 - |q|$ dimensions. The number of such vectors corresponding to the several possible values of $\underline{k}$ is also $2j + 1 - |q|$, and according to Eq. (13-4) these vectors are orthogonal. They will be also orthonormal if we choose to consider the operators $\sqrt{2k + 1}\; u_q^{(k)} = v_q^{(k)}$, which in this as well as other respects are more convenient than the $u_q^{(k)}$. Any matrix $\mathbf{A}_q$ in $2j + 1$ dimensions containing elements only along the q-th parallel to the main diagonal may be expressed in tems of the above vectors.

In the sub-space of the $2j + 1$ basis functions associated with a given value of $j$, the $(2j + 1)^2$ operators $u_q^{(k)}$ for $k \leqslant 2j$ form a complete set. Within that sub-space any operator $T$ may be expanded in terms of the basic set

$$T = \sum_{k=0}^{2j} \sum_{q=-k}^{k} a_{kq} u_q^{(k)} \tag{13-5}$$

The matrix elements of $T$ are given by

$$(j, m+q \mid T \mid jm) = \sum_k a_{kq} (j, m+q \mid u_q^{(k)} \mid jm) \tag{13-6}$$

The coefficients $a_{kq}$ are easily obtained by multiplying both sides by $(j, m+q \mid u_q^{(k')} \mid jm)$, adding over all $m$'s and introducing on the right hand side the orthogonality relations (13-4). One obtains,

$$a_{kq} = (2k+1) \sum_m (j, m+q \mid u_q^{(k)} \mid jm)(j, m+q \mid T \mid jm) \tag{13-7}$$

In general, the coefficients $a_{kq}$ need not be independent of $q$. If they are, the operator $T$ is a sum of irreducible tensor operators $T^{(k)}$ and the coefficients are the corresponding reduced matrix elements. The operators we shall have to consider are usually of this type.

## RELATION BETWEEN THE $u_q^{(k)}$ AND THE ANGULAR MOMENTUM OPERATORS

The operators $u_q^{(k)}$ act on the basis functions as follows

$$u_q^{(k)} \mid jm) = \mid j, m+q) (2j+1)^{-\frac{1}{2}} (jm \, kq \mid j, m+q) \tag{13-8}$$

This immediately suggests that they should be expressible in terms of the angular momentum operators $J_+$, $J_-$, $J_z$ and $J^2$. In particular, they may be conveniently written as a product of the $q$-th power of the m-raising operator $J_+$ (or $J_-$ for negative $q$) and another operator diagonal in this representation, which should therefore be a function of only $J_z$, $J^2$, and the unit operator. We shall write (for $q \geqslant 0$)

$$u_q^{(k)} = (J_+)^q f_{kq} (J^2, J_z) \tag{13-9}$$

The operator $(J_+)^q$ acts on the basis functions according to the well known expression

$$(J_+)^q \, |jm) = |j, \, m+q) \left[ \frac{(j-m)! \, (j+m+q)!}{(j-m-q)! \, (j+m)!} \right]^{\frac{1}{2}}$$

$$= |j, \, m+q) \, f_+ \, (j, \, m, \, q) \qquad (13\text{-}10)$$

while the eigenvalues of the diagonal operator $f_{kq}(J^2, \, J_z)$ are given by the same function $f_{kq}$ of the eigenvalues of $J_z$ and $J^2$,

$$f_{kq}(J^2, \, J_z) \, |jm) = |jm) \, f_{kq} \, (j \, (j+1), \, m) \qquad (13\text{-}11)$$

The explicit form of $f_{kq}$ is most easily determined from the known expression for the coupling coefficients and the equation obtained by introducing Eqs. (13-9), (13-10) and (13-11) into (13-8), that is

$$\sqrt{\frac{1}{2j+1}} \ (j \, m \, k \, q \, | \, j, \, m+q) = f_+ \, (j, \, m, \, q) \, f_{kq} \, (j \, (j+1), \, m) \qquad (13\text{-}12)$$

The expression for the coupling coefficients may be written in the form

$$\sqrt{\frac{1}{2j+1}} \ (j \, m \, k \, q \, | \, j, \, m+q) =$$

$$\left[ \frac{(j-m)! \, (j+m+q)!}{(j-m-q)! \, (j+m)!} \right]^{\frac{1}{2}} \left[ \frac{(2j-k)! \, (k+q)! \, (k-q)!}{(2j+k+1)! \, k! \, k!} \right]^{\frac{1}{2}} \qquad (13\text{-}13)$$

$$\times \sum_\lambda (-1)^{\lambda+k} \begin{pmatrix} k \\ \lambda \end{pmatrix} \begin{pmatrix} k \\ k-q-\lambda \end{pmatrix} \frac{(j+m)! \, (j-m-q)!}{(j+m-\lambda)! \, (j-m-k+\lambda)!}$$

The first factor on the right hand side may be recognized as $f_+$, the remaining ones correspond to $f_{kq}$. The summation is a polynomial in $\underline{j}$ and $\underline{m}$ (of degree $k-q$) which can be rewritten in terms of $j(j+1)$ and $\underline{m}$. These may then be replaced by $J^2$ and $J_z$, respectively to yield the expression for the operator $f_{kq} \, (J^2, \, J_z)$.

The expressions for the $u_q^{(k)}$ operators for $k = 0$, 1, and 2 are given in Table 13-2. Actually, it is more convenient for this purpose to express the operators $u_q^{(k)}$ in a form slightly different from Eq. (13-9), namely

$$u_q^{(k)} = (J_+)^q \, F_{kq}(J^2, \, J_z) \, \sqrt{(2j-k)! \, / \, (2j+k+1)!} \qquad (13\text{-}14)$$

13-4

TABLE 13-2

UNIT TENSOR OPERATORS. SPHERICAL BASIS

$$u_q^{(k)} = (J_+)^q F_{kq}(J^2, J_z) \sqrt{(2j-k)!/(2j+k+1)!}$$

| k | q | $(J_+)^q F_{kq}(J^2, J_z)$ |
|---|---|---|
| 0 | 0 | 1 |
| 1 | 1 | $-\sqrt{2}\, J_+$ |
|   | 0 | $2 J_z$ |
|   | -1 | $\sqrt{2}\, J_-$ |
| 2 | 2 | $\sqrt{6}\, J_+^2$ |
|   | 1 | $-\sqrt{6}\, J_+ (2J_z + 1)$ |
|   | 0 | $2(3J_z^2 - J^2)$ |
|   | -1 | $\sqrt{6}\, J_-(2J_z - 1)$ |
|   | -2 | $\sqrt{6}\, J_-^2$ |

The operators $u_o^{(k)}$ for $k \leq 6$ are given in Table 13-3.

TABLE 13-3

UNIT TENSOR OPERATORS $u_o^{(k)}$ SPHERICAL BASIS

$$u_o^{(k)} = F_{ko}(J^2, J_z) \sqrt{(2j-k)!/(2j+k+1)!}$$

| k | $F_{ko}(J^2, J_z)$ |
|---|---|
| 0 | 1 |
| 1 | $2J_z$ |
| 2 | $2(3J_z^2 - J^2)$ |
| 3 | $4J_z(5J_z^2 - 3J^2 + 1)$ |
| 4 | $2(35J_z^4 - 30J_z^2 J^2 + 3J^4 + 25J_z^2 - 6J^2)$ |
| 5 | $4J_z(63J_z^4 - 70J_z^2 J^2 + 15J^4 + 105J_z^2 - 50J^2 + 12)$ |
| 6 | $4(231J_z^6 - 315J_z^4 J^2 + 105J_z^2 J^4 - 5J^6 + 735J_z^4 - 525J_z^2 J^2 + 40J^4 + 294J_z^2 - 60J^2)$ |

The relation between other operators in spherical basis and the $u_q^{(k)}$ may be established along similar lines. According to Eq. (13-3) the matrix elements of tensor operators between basis functions of the same $\underline{j}$ may be expressed in terms of those for the $u_q^{(k)}$.

Thus, for example, for the matrix elements of the operators corresponding to the spherical harmonics, we have

$$(jm' \mid Y_M^{(L)} \mid jm) = (jm' \mid u_M^{(L)} \mid jm) \, (j \| Y^{(L)} \| j) \tag{13-15}$$

where the reduced matrix elements are given by

$$(j \| Y^{(L)} \| j) = (-1)^j \left[ \frac{2L+1}{4\pi} \right]^{\frac{1}{2}} (2j + 1) \begin{pmatrix} j & L & j \\ 0 & 0 & 0 \end{pmatrix} \tag{13-16}$$

It may be pointed out, however, that the correspondence between the $Y_M^{(L)}$ and the $u_M^{(L)}$ is of a more restricted nature than in the case of the angular momentum operators. On the one hand, the $Y_M^{(L)}$ have non-zero matrix elements between states with different $\underline{j}$ values (satisfying the triangular condition), while the $u_M^{(L)}$ do not, by definition. Thus, although one may write

$$Y^{(L)} = u^{(L)} \, (j \| Y^{(L)} \| j) \tag{13-17}$$

this proportionality relation is only valid within sub-spaces with fixed j-values. On the other hand, the proportionality factors $(j \| Y^{(L)} \| j)$ also vanish for L odd (assuming $\underline{j}$ integral), and therefore the $u_M^{(L)}$ cannot always be expressed in terms of the $Y_M^{(L)}$, unlike the case of the angular momentum operators.

# 14. THE BASIS FUNCTIONS FOR N-ELECTRON SYSTEMS

## THE INDEPENDENT PARTICLE REPRESENTATION

*ANTISYMMETRIC BASIS FUNCTIONS*

The simplest type of basis functions in the N-electron case are the products of N one-electron basis functions. These may be considered as the eigenfunctions of a Hamiltonian of the form

$$H = \sum_{i=1}^{N} H_i \tag{14-1}$$

which corresponds to a system of non-interacting particles. The one-electron basis functions $|a)_i$ for the i-th electron are the eigenfunctions of $H_i$

$$H_i |a)_i = |a)_i E_a \tag{14-2}$$

while the N-electron product functions satisfy

$$H |a)_1 |b)_2 \dots \dots |q)_N = |a)_1 |b)_2 \dots \dots |q)_N (E_a + E_b + \dots + E_q) \tag{14-3}$$

and the energies are additive, as it corresponds to a system of non-interacting particles.

Since the Hamiltonian is a symmetric function of the coordinates of the electrons, it follows that the N! product functions obtained from $|a)_1 |b)_2 \dots |q)_N$ by permutation of electron indices all correspond to the same value of the energy, $E = E_a + E_b \dots + E_q$. This degeneracy does not occur in a physical N-electron system, since the Exclusion Principle asserts that the only states which are allowed are those whose eigenfunctions are antisymmetric under a permutation of any two electrons.

For every set of N different one-electron basis functions there is only one antisymmetric linear combination of product functions, namely the Slater determinant

$$[a\,b\,\dots\dots\,q] = \frac{1}{\sqrt{N!}} \begin{vmatrix} |a)_1 & |a)_2 & \dots\dots & |a)_N \\ |b)_1 & |b)_2 & \dots\dots & |b)_N \\ \dots\dots\dots\dots\dots\dots \\ \dots\dots\dots\dots\dots\dots \\ |q)_1 & |q)_2 & \dots\dots & |q)_N \end{vmatrix} \tag{14-4}$$

We shall designate the N-electron product functions in the form

$$| ab \ldots q) = |a)_1 \, |b)_2 \ldots |q)_N \qquad (14\text{-}5)$$

and use the notation [ab ... q] for the corresponding determinantal wave functions.

The phases of the N-electron product functions are usually taken to be unity, irrespective of the order of their factors. When forming the antisymmetric linear combination of these, [ab ... q], the new overall phase factor is chosen so that a particular product function |ab ... q) has the coefficient +1 in the expansion of the determinant if the one-electron labels appear in some standard order, which has to be specified.

The previous equation (14-4) may also be written in the form

$$[ab \ldots q] = A_N \, | ab \ldots q) \qquad (14\text{-}6)$$

where $A_N$ is the antisymmetrizing operator

$$A_N = \frac{1}{\sqrt{N!}} \; \sum_p (-1)^p \, P \qquad (14\text{-}7)$$

the sum extending over all the operations $P$ of the permutation group of N particles, and $\underline{p}$ is the parity of the corresponding permutation $P$.

The projection operator $\mathbb{P}_N^{(A)}$ for the antisymmetric representation is, according to Eq. (4-14),

$$\mathbb{P}_N^{(A)} = \frac{1}{N!} \; \sum_p (-1)^p \, P \qquad (14\text{-}8)$$

and therefore differs from $A_N$ by a factor $\sqrt{N!}$

$$A_N = \sqrt{N!} \; \mathbb{P}_N^{(A)} \qquad (14\text{-}9)$$

Unlike $\mathbb{P}_N^{(A)}$, the operator $A_N$ is not idempotent, since

$$A_N^2 = \sqrt{N!} \; A_N \qquad (14\text{-}10)$$

14-2

### One-particle Symmetric Operators

The types of operators we shall have to consider in the several-electron problem are symmetric with respect to any interchange of electron indices. According to Eq. (3-9) these operators commute with any permutation P and therefore with the antisymmetrizing operator.

We shall first consider operators of the form

$$F = \sum_{i}^{N} f_i \qquad (14\text{-}11)$$

where the individual $f_i$ operate only on the basis functions of the i-th electron. The $f_i$ operating on a particular product function $|ab \ldots q)$ give

$$f_i |a)_1 |b)_2 \ldots |c)_i \ldots |q)_N = \sum_{c'} |a)_1 |b)_2 \ldots |c')_i \ldots |q)_N (c'|f|c) \qquad (14\text{-}12)$$

or

$$f_i |ab \ldots c \ldots q) = \sum_{c'} |ab \ldots c' \ldots q) (c'|f|c) \qquad (14\text{-}13)$$

where the summation extends to all the one-electron basis functions. The coefficients $(c'|f|c)$ are numbers independent of electron indices.

We can repeat the process for all the $f_i$, add the results and operate with $A_N$ on both sides. Since $A_N$ and F commute, we can write the left-hand side in the form

$$A_N (\Sigma f_i) |ab \ldots q) = F A_N |ab \ldots q) = F [ab \ldots q] \qquad (14\text{-}14)$$

and therefore

$$F [ab \ldots c \ldots q] = \sum_{a'} [a'b \ldots c \ldots q] (a'|f|a) + \ldots$$

$$+ \sum_{c'} [ab \ldots c' \ldots q] (c'|f|c) + \ldots + \sum_{q'} [ab \ldots c \ldots q'] (q'|f|q) \qquad (14\text{-}15)$$

According to this expansion, a symmetric operator of type F connects only states $\psi$ and $\psi'$ which differ at most in one of the labels of the one-electron basis functions. In general, the determinants $[ab \ldots c' \ldots q]$ will not have their labels in the standard order and are therefore related to the corresponding standard determinants $\psi'$ as follows

$$\psi' = (-1)^P [ab \dots c' \dots q] \tag{14-16}$$

where p is the parity of the permutation which transforms one into the other.

If the states $\psi$ and $\psi'$ differ in one label, $c' \neq c$, the matrix elements are given by

$$(\psi'|F|\psi) = (-1)^P ([ab \dots c' \dots q]|F|[ab \dots c \dots q]) = (-1)^P (c'|f|c) \tag{14-17}$$

The diagonal elements are

$$(\psi|F|\psi) = (a|f|a) + \dots + (c|f|c) + \dots + (q|f|q) = \sum_{t=a}^{q} (t|f|t) \tag{14-18}$$

since each of the summations on the right in (14-15), for $a' = a, \dots, c' = c, \dots, q' = q$, respectively, contributes to the coefficient of $[ab \dots c \dots q]$.

### Two-particle Symmetric Operators

Another important class of symmetric operators of interest in atomic problems are of the form

$$G = \sum_{i > j}^{N} g_{ij} \tag{14-19}$$

where the $g_{ij}$ operate only on the basis functions of the i-th and j-th electrons.

Following the same argument as in the case of $F = \Sigma f_i$, we arrive at the expression

$$G [ab \dots c \dots e \dots q] =$$

$$= \sum_{a', b'} [a' b' \dots c \dots e \dots q] (a'b'|g|ab) + \dots$$

$$+ \sum_{c', e'} [ab \dots c' \dots e' \dots q] (c'e'|g|ce) + \dots \tag{14-20}$$

and therefore a symmetric operator of type G connects only states $\psi$ and $\psi'$ which differ at most in two of the labels of their one electron basis functions. The same remarks as before apply in reference to the relative phases of the $\psi$'s and the determinants on the right-hand side.

In every summation in Eq. (14-20) both indices assume all possible values, and for every pair of values $c'$ and $e'$ there are two terms for which the determinants are not independent, namely

$$[ab \ldots c' \ldots e' \ldots q] \, (c'e'|g|ce) + [ab \ldots e' \ldots c' \ldots q](e'c'|g|ce) \qquad (14\text{-}21)$$

Since one determinant is the negative of the other, and for $c' = e'$ they vanish, we may replace the summations in Eq. (14-20) by sums over pairs $c' > e'$ in the form

$$G [ab \ldots c \ldots e \ldots q] =$$

$$= \sum_{a' > b'} [a'b' \ldots c \ldots e \ldots q] \, \{(a'b'|g|ab) - (b'a'|g|ab)\} + \ldots$$

$$+ \sum_{c' > e'} [ab \ldots c' \ldots e' \ldots q] \, \{(c'e'|g|ce) - (e'c'|g|ce)\} + \ldots \qquad (14\text{-}22)$$

If the states $\psi$ and $\psi'$ differ in two labels, $c' \neq c$, and $e' \neq e$, the matrix elements of G are given by

$$(\psi'|F|\psi) = (-1)^P \, ([ab \ldots c' \ldots e' \ldots q] \, |G| [ab \ldots c \ldots e \ldots q])$$

$$= (-1)^P \, \{(c'e'|g|ce) - (e'c'|g|ce)\} \qquad (14\text{-}23)$$

If $\psi$ and $\psi'$ differ only by one label, $c' \neq c$, every sum over pairs $c' > a'$, $c' > b'$, ..., $c' > q'$ contributes to the coefficient of $[ab \ldots c' \ldots q]$ when $a' = a$, $b' = b$, ..., $q' = q$, respectively. The matrix elements are therefore

$$(\psi'|G|\psi) = (-1)^P \, ([ab \ldots c' \ldots q] \, |G| [ab \ldots c \ldots q])$$

$$= (-1)^P \sum_{t=a}^{q} \, \{(c't|g|ct) - (tc'|g|ct)\} \qquad (14\text{-}24)$$

If $\psi = \psi'$, all the summations contribute to the coefficient of $[ab \ldots q]$ when the primed indices are equal to a, b, ..., q, and the diagonal elements are given by the double sum

$$(\psi|G|\psi) = \sum_{k > t = a}^{q} \, \{(kt|g|kt) - (tk|g|kt)\}, \qquad (14\text{-}25)$$

14-5

Within the independent-particle scheme the one-electron basis functions may be chosen in different ways, depending on the particular form of the one-electron Hamiltonian $H_i$, of which the $|a\rangle_i$ are the eigenfunctions.

When considering free atoms or ions these basis functions are usually chosen to be the eigenfunctions of a one-electron Hamiltonian of the form

$$H_i = \frac{1}{2\mu}\, p_i^2 + u(r_i) \tag{14-26}$$

In this "central-field" scheme, the one-electron basis functions are characterized by the familiar quantum numbers $\underline{n}\,\underline{\ell}\,m_s\,m_\ell$. The eigenvalues of such a Hamiltonian depend only on the quantum numbers $\underline{n}$ and $\underline{\ell}$, since $H_i$ is independent of the spin or spatial orientation. It therefore has a high degree of degeneracy, since all the states of the same configuration have the same energy.

The so-called "strong-field" scheme is often used when considering ions in crystal lattices. In this case the one-electron basis functions are eigenfunctions of a one-electron Hamiltonian of the type

$$H_i = f_A(\theta_i, \phi_i) \tag{14-27}$$

which is a symmetric function under the operations of the pertinent crystallographic point group.

In the central-field scheme our choice of standard order for the determinantal basis functions is that where the N sets of quantum numbers $\underline{n}\,\underline{\ell}\,m_s\,m_\ell$ of the one-electron functions are listed in dictionary order according to increasing values of $\underline{n}$ and $\underline{\ell}$, but decreasing values of $m_s$ and $m_\ell$. This differs from the standard order in Condon and Shortley[9], which is really according to $n\,\ell\,m_\ell\,m_s$, so that in their case the ordering by $m_\ell$ values precedes the ordering by $m_s$ values.

Each set of $\underline{n}\,\underline{\ell}$ values labels a shell. The list of all sets of $\underline{n}\,\underline{\ell}$ values, each with a superscript indicating the number of electrons in the shell, specifies a configuration. The states of a configuration are described by listing also the $m_s$ and $m_\ell$ values of the electrons in the incomplete shells. For these, the several $m_\ell$ values corresponding to $m_s = \frac{1}{2}$ are given inside parenthesis labelled by an upper + sign, then the $m_\ell$ for $m_s = -\frac{1}{2}$ in a

parenthesis labelled by a minus sign. For example, a state of a configuration of $Cr^{++}$ is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 \ [21, -1]^+ [-1]^-$$

In order to simplify the notation and use only the minimum necessary number of labels, it is customary to retain only those which are relevant to the problem under consideration. Thus, for example, when considering only states of the $Cr^{++}$ ion in the given configuration, it is only necessary to specify the $m_s \ m_\ell$ values of the four d-electrons in the incomplete shell, and those will be written simply in the form $[21, -1]^+ [-1]^-$, $[210]^+ [-2]^-$, etc.

In later Sections we shall use a still simpler notation. If only states where all the $m_s$ values are $+\frac{1}{2}$ are considered, we shall write a symbol $[210]^+$ as $[210]$. Similarly a symbol like $[21, -1]^+ [-1]^-$ will be replaced by $[21\bar{1}|\bar{1}]$.

# 15. THE BASIS FUNCTIONS FOR N-ELECTRON SYSTEMS

## THE LS-COUPLING SCHEME

The independent-particle Hamiltonian previously considered is not a good approximation to the true Hamiltonian of an atomic system of several electrons. It does not include terms which make a significant contribution to the energy of the system. If the terms corresponding to the Coulomb repulsion of the electrons and the spin-orbit coupling energy are included, the Hamiltonian for a free atom or ion takes the form

$$H = \sum_{i}^{N} \left( \frac{1}{2\mu} p_i^2 - \frac{Z e^2}{r_i} + \xi(r_i) \, l_i \cdot s_i \right) + \sum_{i>j}^{N} \frac{e^2}{r_{ij}} \tag{15-1}$$

It is found that in practice this constitutes a rather good approximation to the true Hamiltonian. Experimental results also show that the spin-orbit coupling energy is usually small compared to the other terms.

If the spin-orbit coupling terms are excluded, the resultant Hamiltonian is spin-independent, and is therefore invariant under rotations in the coordinate space as well as in the spin space. It is therefore convenient to choose a system of N-electron basis functions classified according to the different irreducible representations of these rotation groups. This is equivalent to a classification according to the different eigenvalues of the commuting operators $L^2, S^2, L_z$, and $S_z$. The vector operators $L$ and $S$ correspond to the total orbital and spin angular momentum, respectively, and are given by

$$L = l_1 + l_2 + \ldots + l_N$$

$$S = s_1 + s_2 + \ldots + s_N \tag{15-2}$$

where the $l_i$ and $s_i$ are the corresponding operators for the individual electrons. The operators $L^2$ and $S^2$ are

$$L^2 = (L \cdot L) = \frac{1}{2} (L_+ L_- + L_- L_+) + L_z^2$$

$$S^2 = (S \cdot S) = \frac{1}{2} (S_+ S_- + S_- S_+) + S_z^2 \tag{15-3}$$

The basis functions in this representation are characterized by the corresponding quantum numbers and written in the form $| \alpha S L M_S M_L )$. The symbol $\alpha$ stands for all the rest of the indices or quantum numbers necessary to specify the state, such as the configuration, etc.

According to the properties of symmetric operators, Eq. (3-19), in this representation the Hamiltonian of the free ion (with no spin-orbit terms) has zero matrix elements between basis functions which differ in any of the quantum numbers $S L M_S M_L$.

## CONFIGURATIONS OF EQUIVALENT ELECTRONS

When considering the configurations of several equivalent electrons it is often found that there are several states with the same set of quantum numbers $S L M_S M_L$ for a given configuration. The simplest case when this occurs is for the $d^3$ configuration, to which two $^2D$ states belong. According to the arguments given in Section 8, it is convenient to classify these states according to the eigenvalues of other operator or set of operators which commute with the previous $L^2$, $S^2$, $L_z$, and $S_z$.

For the configurations of several d-electrons, $(\ell = 2)$, the appropriate operator is

$$G(R_5) = 3 [U^{(1)}]^2 + 7[U^{(3)}]^2 \qquad (15\text{-}4)$$

For the configurations of several f-electrons, $(\ell = 3)$ there are two operators of that sort

$$G(G_2) = 3[U^{(1)}]^2 + 11[U^{(5)}]^2 \qquad (15\text{-}5)$$

$$G(R_7) = 3[U^{(1)}]^2 + 7[U^{(3)}]^2 + 11[U^{(5)}]^2 \qquad (15\text{-}6)$$

The $U^{(k)}$ are the N-electron operators corresponding to the unit operators $u^{(k)}$ discussed in Section 13,

$$U^{(k)} = \sum_i^N u^{(k)}(i) \qquad (15\text{-}7)$$

and may be expressed in terms of the angular momentum operators, as previously indicated. In particular, the operator $U^{(1)}$ is proportional to the total orbital angular momentum operator $L$.

15-2

In the same way that a classification of the basis functions according to the eigenvalues of $L^2$, or $[U^{(1)}]^2$, is equivalent to that according to the different irreducible representations of the rotation group in three dimensions, $R_3$, the classification according to the eigenvalues of $G(R_5)$ or $G(R_7)$ is equivalent to that according to the irreducible representations of the groups designated as $R_5$ and $R_7$, respectively. These are rotation groups in the space of the $2\ell + 1$ basis functions for d- or f-electrons. The group designated as $G_2$ is a subgroup of $R_7$. The three-dimensional rotation group $R_3$ is a subgroup of all of these. We shall discuss these questions at greater length in the Appendix. At this point we shall only indicate the basic facts which are relevant to the forthcoming discussions.

The irreducible representations of $R_5$ are characterized by two integers $\lambda_1 \geqslant \lambda_2$ and symbolized by $(\lambda_1\lambda_2)$. The corresponding eigenvalues of the operator $G(R_5)$ are a function of $\lambda_1$ and $\lambda_2$

$$G_5(\lambda_1,\lambda_2) = \frac{1}{2} [\lambda_1(\lambda_1 + 3) + \lambda_2(\lambda_2 + 1)] \qquad (15\text{-}8)$$

The irreducible representations of $R_5$ which are of interest in the classification of the states of the $d^N$ configurations are given in Table 15-2. This also shows the reduction of these representations into those of $R_3$.

The irreducible representations of the group $R_7$ are characterized by three integers $\lambda_1 \geqslant \lambda_2 \geqslant \lambda_3$ and symbolized by $(\lambda_1\lambda_2\lambda_3)$. The eigenvalues of the operator $G(R_7)$ for the eigenfunctions of the representation $(\lambda_1\lambda_2\lambda_3)$ are

$$G_7(\lambda_1,\lambda_2,\lambda_3) = \frac{1}{2} [\lambda_1(\lambda_1 + 5) + \lambda_2(\lambda_2 + 3) + \lambda_3(\lambda_3 + 1)] \qquad (15\text{-}9)$$

The representations of the subgroup $G_2$ are characterized by two integers $\mu_1 \geqslant \mu_2$, and also symbolized by $(\mu_1\mu_2)$. The eigenvalues of the operator $G(G_2)$ for the basis functions of the $(\mu_1\mu_2)$ representation are given by

$$G_2(\mu_1,\mu_2) = \frac{1}{3} [\mu_1(\mu_1 + 5) + \mu_2(\mu_2 + 4) + \mu_1\mu_2] \qquad (15\text{-}10)$$

The irreducible representations of $R_7$ and $G_2$ which are of interest in the classification of the states of the $f^N$ configurations are given in Tables 15-3 to 15-7. These also show the reduction of the irreducible representations of $R_7$ into those of $G_2$, and these in turn into representations of $R_3$.

15-3

*The* $|g\,S\,L\,M_S M_L\,)$ *Functions*

The vector-coupling methods described in previous Sections require some modifications when applied to the determination of the N-electron basis functions in LS-coupling, on account of the antisymmetry requirements. There are essentially two methods of approach. One starts with antisymmetric N-electron basis functions in the independent-particle representation, and determines linear combinations of these which are $|S\,L\,M_S M_L\,)$ basis functions. The other approach starts constructing $|S\,L\,M_S M_L\,)$ basis functions by use of the vector coupling methods and then the appropriate linear combinations of these which are antisymmetric for interchange of electrons. Both methods have their own virtues and disadvantages. The first involves simpler types of arguments and we shall consider it in the present Section.

We shall describe the method for $n\,\ell^N$ configurations of equivalent electrons. The extension to those consisting of two or more incomplete shells presents no additional difficulties. In its simplest form, the method was used by Gray and Wills[10]. We shall also show how it can be modified and extended to obtain $|S\,L\,M_S M_L\,)$ basis functions which are also eigenfunctions of the operators $G(R_{2\ell+1})$ and $G(G_2)$, which we shall call $|g\,S\,L\,M_S M_L\,)$

In this method the eigenfunction $|g\,S\,L\,M_S M_L\,)$ for the highest $M_S$ and $M_L$, namely $M_S = S$ and $M_L = L$ for each state is found by orthogonality considerations. The eigenfunctions for the other possible values of $M_S$ and $M_L$ may then be found by repeated application of the lowering operators $S_-$ and $L_-$.

In order to form the $|g\,S\,L\,M_S M_L\,)$ linear combinations we shall need to know the effect of operating with $S_-, L_-$ and $U_q^{(k)}$ on the determinantal basis functions. Since all these operators are of the type $F = \sum_i f_i$, the results are given by Eq. (14-15).

For simplicity, the basis functions of the previous Section will be written in the form

$$[m_{\ell_1} m_{\ell_2} \dots m_{\ell_r} | m_{\ell_{r+1}} \dots m_{\ell_N}] \tag{15-11}$$

where the $m_{\ell_i}$ values listed on the left of the vertical bar correspond to $m_s = \frac{1}{2}$, those on the right to $m_s = -\frac{1}{2}$. If they all correspond to $m_s = \frac{1}{2}$ they will be written as

$$[m_{\ell_1} m_{\ell_2} \dots m_{\ell_r}] \tag{15-12}$$

with $r = N$.

The application of $L_-$ to one of these is given by

$$L_-[m_{l_1} \cdots m_{l_i} \cdots | \cdots m_{l_N}] = \sum_{m_{l_i}} [m_{l_1} \cdots m_{l_i}-1 \mid \cdots m_{l_N}] \sqrt{(\ell + m_{l_i})(\ell - m_{l_i} + 1)}$$

(15-13)

Similarly, for $S_-$ we obtain

$$S_-[m_{l_1} \cdots m_{l_i} \cdots | \cdots m_{l_N}] = \sum_{m_{l_i}} [m_{l_1} \cdots | \cdots m_{l_i} \cdots m_{l_N}] (-1)^p$$

(15-14)

For the operators $U_q^{(k)}$, according to Eq. (13-8) we obtain the following result

$$U_q^{(k)}[m_{l_1} \cdots m_{l_i} \cdots | \cdots m_{l_N}] = \sum_{m_{l_i}} [m_{l_1} \cdots m_{l_i}+q \cdots | \cdots m_{l_N}](-1)^p \frac{(\ell\, m_{l_i} kq \mid \ell, m_{l_i} + q)}{\sqrt{2\ell + 1}}$$

(15-15)

As indicated previously, p is the number of interchanges necessary to bring the resulting $m_{l_i}$ + q value to its place, so that in the final determinant all the $m_l$ values be ordered in descending order. If the new $m_{l_i}$ + q value is the same as any of the other $m_{l_j}$ values for the same $m_s$, the corresponding determinantal function vanishes.

In the actual performance of the operations it is advantageous to use some diagrams where the matrix elements on the right- hand side of Eqs. (15-13) and (15-15) are shown connecting the corresponding $m_{l_i}$ values. This allows the effect of an operator on the basis functions to be determined by inspection.

For example, when considering configurations of equivalent d-electrons, $(\ell = 2)$, we have the following diagram for $L_-$



(15-16)
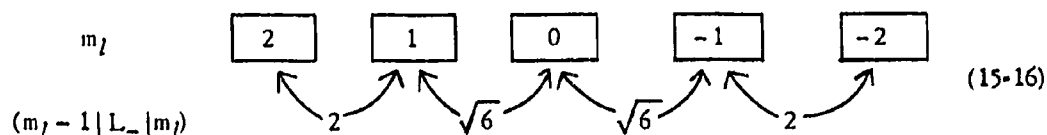
With the help of this diagram, the effect of $L_-$ on a determinant such as [20|1] is easily found to be

$$L_-[20|1] = \sqrt{6}\,[20|0] + \sqrt{6}\,[2\bar{1}|1] + 2[10|1]$$

(15-17)

Similarly, the corresponding diagrams for the operators $U_{-1}^{(3)}$, $U_{-2}^{(3)}$, and $U_{-3}^{(3)}$ are

$m_l$



$a(m_l - 1|U_{-1}^{(3)}|m_l)$

(15-18)

$m_l$



$a(m_l - 2|U_{-2}^{(3)}|m_l)$

(15-19)

$m_l$



$a(m_l - 3|U_{-3}^{(3)}|m_l)$

(15-20)
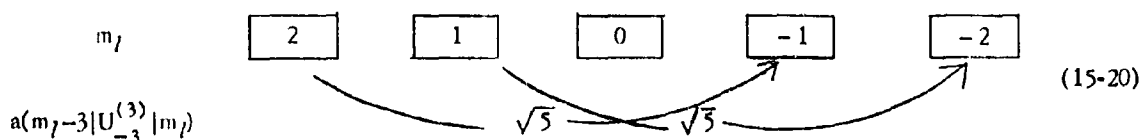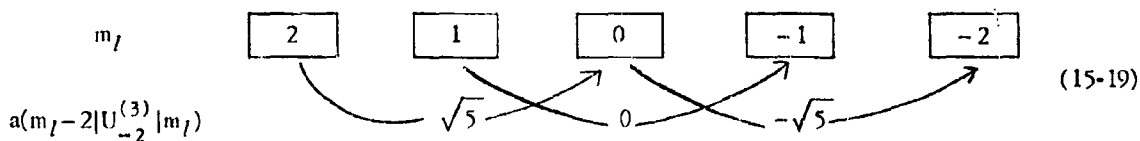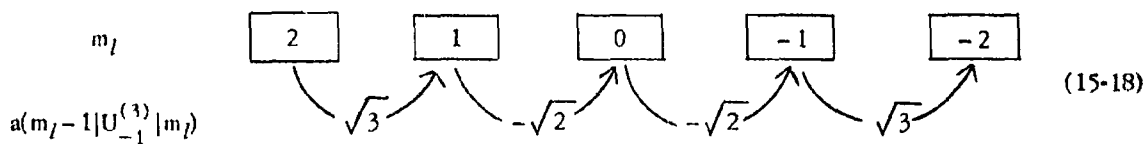
All the matrix elements have been multiplied by the constant $\underline{a} = \sqrt{2 \cdot 5 \cdot 7}$ to avoid denominators. A constant factor may always be omitted, since normalization is easily accomplished. For example, the operation of $U_{-2}^{(3)}$ on $[21|0]$ is

$$U_{-2}^{(3)}\ [21|0] = \frac{\sqrt{5}}{a}\ \{-[21|\bar{2}] + 0[2\bar{1}|0] + [01|0]\}$$

(15-21)

$$= \frac{\sqrt{5}}{a}\ \{-[21|\ddot{2}] - [10|0]\}$$

The effect of $S_-$ on a determinantal basis function requires only to consider the permutation factor $(-1)^P$. Thus, for example,

$$S_-[210\bar{1}] = [210|\bar{1}] - [21\bar{1}|0] + [20\bar{1}|1] - [10\bar{1}|2]$$

(15-22)

The determinantal basis functions are already eigenfunctions of $L_z$ and $S_z$ with eigenvalues given by

$$M_L = \sum_i m_{l_i}$$

$$M_S = r - \frac{N}{2}$$

(15-23)

15-6

In the process of determining the $|g\,S\,L\,M_S M_L)$ functions according to the present method, it is convenient, though not always necessary, to obtain first those for the highest value of the total spin S, and proceed to those for $S = N/2 - 1, \ldots, 1/2$ or 0, successively. It is only necessary for most purposes to determine one function for every set of values $g\,S\,L$, and the simplest one is usually the function $|g\,S\,L\,S\,L)$ with the highest values of $M_S$ and $M_L$. The remaining ones may be obtained by repeated operation with $S_-$ and $L_-$.

For a given value of S, there is only one determinant with $M_S = S$ and largest $M_L$, and this must correspond to the function $|S\,L_H S\,L_H)$ of the state with the highest L for that multiplicity.

Operating with $L_-$ on this function one obtains the function $|S\,L_H S, L_H - 1)$. If this is a linear combination of $\underline{n}$ determinants, the remaining $n - 1$ linear combinations of these, orthogonal to the previous one, must correspond to states with $L = L_H - 1$. Those belonging to states of higher total spin may be assumed to be known from a previous stage. The rest are $|S, L_H - 1, S, L_H - 1)$ functions. If there is more than one, they can be determined so that they be also eigenfunctions of the $G$ operators of Eqs. (15.4) to (15-6). The appropriate orthogonality conditions are described below.

The operator $L_-$ may be applied to these functions with $M_L = L_H - 1$ and the whole process repeated until finally the functions with the lowest value of L are obtained. It should be pointed out that it is not necessary to operate with $L_-$ on the actual linear combinations of determinants obtained at a given stage, but only on the determinants themselves, since this provides equivalent, but simpler, orthogonality relations to be satisfied by the new $|S\,L\,M_S M_L)$ functions to be determined at the next stage.

The additional orthogonality conditions necessary to obtain $|S\,L\,M_S M_L)$ functions which are also eigenfunctions of the $G$ operators are obtained by use of the $U_q^{(k)}$ operators. We shall consider first the case of the $d^N$ configurations. The corresponding operator $G(R_5)$ is

$$G(R_5) = 3[U^{(1)}]^2 + 7[U^{(3)}]^2 \tag{15-21}$$

Since $U^{(1)}$ is proportional to $\mathbf{L}$, in a representation where $L^2$ and $G(R_5)$ are diagonal the operator $[U^{(3)}]^2$ must also be diagonal. Accordingly, the operators $U_q^{(3)}$ acting on a function that belongs to a given irreducible representation $(\lambda_1 \lambda_2)$ of $R_5$ can only give functions which belong to the same irreducible representation, and which are therefore orthogonal to all those belonging to others. A familiar analog is afforded by $L_+$, $L_z$, and $L_-$, which operate on $|L\,M_L)$ eigenfunctions to give only others with the same L value.

In the case of the $f^N$ configurations, the two operators to be considered are

$$\mathcal{G}(G_2) = 3[\mathbf{U}^{(1)}]^2 + 11[\mathbf{U}^{(5)}]^2$$

and

$$\mathcal{G}(R_7) = \mathcal{G}(G_2) + 7[\mathbf{U}^{(3)}]^2$$

(15-22)

The same arguments used in the case of $R_5$ show that in a representation where $L^2$, $\mathcal{G}(G_2)$ and $\mathcal{G}(R_7)$ are diagonal, all three operators $[\mathbf{U}^{(1)}]^2$, $[\mathbf{U}^{(3)}]^2$, and $[\mathbf{U}^{(5)}]^2$ are also diagonal. The operators $U_q^{(5)}$ connect only functions belonging to the same irreducible representation $(\mu_1\mu_2)$ of $G_2$, while the operators $U_q^{(3)}$ connect only functions of the same irreducible representation $(\lambda_1\lambda_2\lambda_3)$ or $R_7$.

The process of determining the eigenfunctions of the $L^2, S^2$, and $\mathcal{G}$ operators is facilitated by the knowledge of the number of states to be expected and their classification according to the eigenvalues of these operators (or the irreducible representations of the corresponding groups). This knowledge can be gained by group-theoretical considerations.[11,12] This classification for the $d^N$ and $f^N$ configurations is given in Tables 15-2 to 15-7.

## THE HALF-SHELL RULE

There is a very important rule which allows the determination of $|g\,S\,L\,M_S\,M_L)$ eigenfunctions for many states of configurations of several electrons from those with a smaller number of electrons and vice versa. The considerable simplification that it introduces reduces the labor involved by approximately a half.

Let us consider two determinantal basis functions for a given configuration of equivalent electrons which differ only on one of the $m_l$ values

$$A = [m_{l_1} \cdots m_{l_a} \cdots m_{l_r}| \cdots m_{l_N}] \qquad A' = [m_{l_1} \cdots m_{l_a'} \cdots m_{l_r}| \cdots m_{l_N}] \quad (15\text{-}23)$$

Next consider the determinants of the configuration of $N'$ electrons ($N' = 2\ell + 1 + N - 2r$) obtained from the previous ones by replacing holes in the $m_s = \frac{1}{2}$ half-shell by electrons with the negatives of their corresponding $m_l$ values. Thus, for example, if we take the above determinants to be $[32|1]$ and $[30|1]$ of the $f^3$ configuration, and represent them schematically in the form

$A$

| 3 | 2 |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | 1 |  |  |  |  |

$A$

| 3 |  |  | 0 |  |  |  |
|---|---|---|---|---|---|---|
|  |  | 1 |  |  |  |  |

(15-24)

the associated determinants for $f^6$ obtained by the above rule are $[3210\bar{1}|1]$ and $[321\bar{1}\bar{2}|1]$, respectively

$\overline{A}$

| 3 | 2 | 1 | 0 | $\bar{1}$ |  |  |
|---|---|---|---|---|---|---|
|  |  | 1 |  |  |  |  |

$\overline{A}'$

| 3 | 2 | 1 |  | $\bar{1}$ | $\bar{2}$ |  |
|---|---|---|---|---|---|---|
|  |  | 1 |  |  |  |  |

(15-25)

It is easily seen that the determinant of $N'$ electrons associated to A will contain the quantum number $-m_{l_{a'}}$, the one associated to $A'$ will contain $-m_{l_a}$, while the rest of the $m_l$ will be common to both.

The matrix element of a tensor operator $U_q^{(k)}$ (with $q \neq 0$) between the determinantal basis functions $A$ and $A'$ is, according to Eq. (14-17)

$$(A'|U_q^{(k)}|A) = (-1)^p (\ell, m_{l_{a'}}|u_q^{(k)}|\ell, m_{l_a})$$ (15-26)

The corresponding matrix element between the "half-shell associate" determinants, $\overline{A}$ and $\overline{A}'$, is

$$(\overline{A}'|U_q^{(k)}|\overline{A}) = (-1)^{\overline{p}} (\ell, -m_{l_a}|u_q^{(k)}|\ell, -m_{l_{a'}})$$ (15-27)

It is easily proved that the parities $p$ and $\overline{p}$ of the pertinent permutations satisfy

$$\overline{p} = p + |q| - 1 \quad \text{for } q \neq 0; \qquad \overline{p} = p \quad \text{for } q = 0$$ (15-28)

The symmetry relations between the matrix elements of the $u_q^{(k)}$ operators are

$$(\ell, -m|u_q^{(k)}|\ell, -m') = (-1)^{k-q}(\ell m'|u_q^{(k)}|\ell m)$$ (15-29)

From all these considerations, it follows that

$$(\overline{A}'|U_q^{(k)}|\overline{A}) = (-1)^{k-1}(A'|U_q^{(k)}|A)$$ (15-30)

This relation is also valid without modification for $q = 0$ in the case of $k$ odd, since

$$\sum_m (\ell m | u_0^{(k)} | \ell m) = 0, \text{ for } k \text{ odd} \tag{15-31}$$

All previous considerations used in the determination of the $|g SL M_S M_L)$ functions, with the exception of those concerning the spin, make use of the operators $U_q^{(1)}$, $U_q^{(3)}$ and $U_q^{(5)}$, which act in identical fashion on "half-shell associate" determinants.

It follows that if a linear combination of determinants belongs to given irreducible representations of $R_3$ and $R_5$ (or $R_3$, $G_2$ and $R_7$), the corresponding linear combination of the "half-shell associate" determinants also belongs to the same representations. It must be noticed, however, that they correspond to different $S$ and $M_S$ eigenvalues.

Thus, for example, if the $|g SL M_S M_L)$ basic functions for $f^2$ are known, the corresponding functions belonging to the representations (000) (200) and (110) for other configurations $f^5$, $f^4$, $f^6$, $f^7$ may be obtained by the "half-shell rule" and by appropriate use of the $S_-$ operator. One example of the use of this rule is given below for the $d^3$ configuration

*Example: The $d^3$ Configuration*

We shall illustrate the method by obtaining one basis function, $M_L = L$ and $M_S = S$, for each of the states of the $d^3$ configuration.

The basis function for the quartet states $^4F$ and $^4P$ may be obtained from those for the triplet states of $d^2$ by use of the "half-shell rule",

$$d^2 \qquad ^3F = [21] \qquad ^3P = \{ \sqrt{2}\,[2\bar{1}] - \sqrt{3}\,[10] \} / \sqrt{5} \tag{15-32}$$

$$d^3 \qquad ^4F = [210] \qquad ^4P = \{ \sqrt{2}\,[20\bar{1}] - \sqrt{3}\,[212] \} / \sqrt{5} \tag{15-33}$$

For the doublet states, we start with the one with the highest L, namely the $^2H$. There is only one wave function with $M = 5$, and this must correspond to $^2H$

$$^2H = [21|2] \tag{15-34}$$

If the M-lowering operator is applied to this, we obtain a linear combination of two functions $[21|1]$ and $[20|2]$, which corresponds to $^2H$, $M_L = 4$.

The other independent linear combination, orthogonal to the previous one must correspond to a new state, namely the G. The process is facilitated by adopting a scheme of the type

|              | $[21|1]$   | $[20|2]$ |
| ------------ | ---------- | -------- |
| $L_-[21|2]$  | 2          | $\sqrt{6}$ |
| $^2G$        | $\sqrt{6}$ | $-2$     |

$$\tag{15-35}$$

The first row is actually the matrix of the $L_-$ operator. The last row gives the coefficients of the function corresponding to the $^2G$ state. If this is normalized, we can write it in the form

$$^2G = \{ \sqrt{3}\,[21|1] - \sqrt{2}\,[20|2] \} / \sqrt{5} \tag{15-36}$$

We may proceed in the same form now, and apply $L_-$ to the previous functions. Since we are not interested in the $M_L = 3$ functions for the $^2H$ and $^2G$ states, we may apply $L_-$ to the functions $[21|1]$ and $[20|2]$ rather than to the linear combinations corresponding to the

$M_L = 4$ functions of the $^2H$ and $^2G$ states. This not only avoids a matrix multiplication, but also simplifies the determination of the basis functions for the new states making their appearance at this point. The new functions must be orthogonal to any linear combination of the $M_L = 3$ functions for $^2H$ and $^2G$, and therefore to $L_- [21|1]$ and $L_- [20|2]$. The matrix of $L_-$ between determinantal basis functions may be obtained by inspection by means of the diagrams (15-16).

The calculation scheme for $M_L = 3$ is

|  | [21\|0] | [20\|1] | [2$\bar{1}$\|2] | [10\|2] |
|---|---|---|---|---|
| $L_-$ [21\|1] | $\sqrt{6}$ | $\sqrt{6}$ | 0 | 0 |
| $L_-$ [20\|2] | 0 | 2 | $\sqrt{6}$ | 2 |
| $^4F$ | 1 | −1 | 0 | 1 |
| $^2F$ | 1 | −1 | $\sqrt{6}$ | −2 |

(15-37)

The two first rows constitute the matrix of $L_-$. There are now four basis functions for $M_L = 3$ and therefore two new basis functions for F states. One of these must be the $M_S = \frac{1}{2}$ function of the $^4F$ state, which may be obtained from the already known $M_S = 3/2$ function [210] as $S_- [210]$, and is given in the third row.

The remaining function corresponds to the new $^2F$ state. Its coefficients are given in the last row, which is orthogonal to all the others.

We shall carry the process one step further and work out the scheme for the $M_L = 2$ functions. This is of interest, because in this case we obtain two states of the same type, namely two $^2D$ states, and we shall show how they can be chosen to belong to different representations of the group $R_5$.

The calculation scheme for the $M_L = 2$ functions is

|  | [21\|$\bar{1}$] | [20\|0] | [2$\bar{1}$\|1] | [10\|1] | [2$\bar{2}$\|2] | [1$\bar{1}$\|2] |
|---|---|---|---|---|---|---|
| $L_-$ [21\|0] | $\sqrt{6}$ | $\sqrt{6}$ | 0 | 0 | 0 | 0 |
| $L_-$ [20\|1] | 0 | $\sqrt{6}$ | $\sqrt{6}$ | 2 | 0 | 0 |
| $L_-$ [2$\bar{1}$\|2] | 0 | 0 | 2 | 0 | 2 | 2 |
| $L_-$ [10\|2] | 0 | 0 | 0 | 2 | 0 | $\sqrt{6}$ |
| $^2D_{(10)}$ | 1 | −1 | 1 | 0 | −1 | 0 |
| $^2D_{(21)}$ | −3 | 3 | 1 | −2$\sqrt{6}$ | −5 | 4 |

(15-38)

15-12

After the matrix elements of $L_-$ have been determined, the $^2D_{(10)}$ function may be found in essentially two different ways which we shall sketch briefly.

The first method makes use of the fact that the $^5D_{(10)}$ function of the $d^4$ configuration also belongs to the (10) representation of $R_5$. The $^5D_{(10)}$ function for $M_L = 2$, $M_S = S = 2$, is simply [2101]. The function for $M_S = 1$ is easily obtained as

$$S_- [210\bar{1}] = [210|\bar{1}] - [21\bar{1}|0] + [20\bar{1}|1] - [10\bar{1}|2] \tag{15-39}$$

The $^2D_{(10)}$ function for $d^3$ is obtained from this by means of the "half-shell rule".

Another method is based on the fact that the $U^{(3)}$ operators connect only states of the same irreducible representation of $R_5$. Since the determinantal basis function for $M \geqslant 3$ do not form functions of the (10) representation, the operators $U_q^{(3)}$ operating on them will always yield functions orthogonal to those of the $^2D_{(10)}$ state. We can take, for example

$$U_{-3}^{(3)} [21|2] = N \{ [21|\bar{1}] + [2\bar{2}|2] - [1\bar{1}|2] \} \tag{15-40}$$

The coefficients for the $^2D_{(10)}$ function may then be determined by this additional orthogonality condition.

Finally, the function for the $^2D_{(21)}$ state is obtained by making it orthogonal to that for $^2D_{(10)}$ and the $L_- [21|0]$, etc.

# TABLE 15-1

## STATES OF THE $p^n$ CONFIGURATIONS

| N | 2S+1 | L |
|---|------|---|
| 1 | 2 | P |
| 2 | 3 | P |
|   | 1 | S   D |
| 3 | 4 | S |
|   | 2 | PD |

TABLE 15-2

STATES OF THE $d^n$ CONFIGURATIONS

| N | 2S+1 | R5 | R3 |
|---|------|-----|-----|
| 1 | 2 | (10) | D |
| 2 | 3 | (11) | P F |
|   | 1 | (00) (20) | S D G |
| 3 | 4 | (11) | P F |
|   | 2 | (10) (21) | D PDFGH |
| 4 | 5 | (10) | D |
|   | 3 | (11) (21) | P F PDFGH |
|   | 1 | (00) (20) (22) | S D G S DFG I |
| 5 | 6 | (00) | S |
|   | 4 | (11) (20) | P F D G |
|   | 2 | (10) (21) (22) | D PDFGH S DFG I |

## TABLE 15-3a

## STATES OF THE $f^2$ CONFIGURATION

| N | 2S+1 | R7 | G2 | R3 |
|---|------|-----|--------------|---------|
| 2 | 3 | 110 | (10)<br>(11) | F<br>P   H |
|   | 1 | 000 | (00) | S |
|   |   | 200 | (20) | D G I |

## TABLE 15-3b

## STATES OF THE $f^3$ CONFIGURATION

| N | 2S+1 | R7 | G2 | R3 |
|---|------|-----|----------------------|-------------------------|
| 3 | 4 | 111 | (00)<br>(10)<br>(20) | S<br>F<br>D G I |
|   | 2 | 100 | (10) | F |
|   |   | 210 | (11)<br>(20)<br>(21) | P   H<br>D G I<br>DFGH KL |

# TABLE 15-4

## STATES OF THE $f^4$ CONFIGURATION

| N | 2S+1 | R7 | G2 | R3 |
|---|------|-----|------|-----|
| 4 | 5 | 111 | (00) | S |
|   |   |   | (10) | F |
|   |   |   | (20) | D G I |
|   | 3 | 110 | (10) | F |
|   |   |   | (11) | P H |
|   |   | 211 | (10) | F |
|   |   |   | (11) | P H |
|   |   |   | (20) | D G I |
|   |   |   | (21) | DFGH KL |
|   |   |   | (30) | P FGHIK M |
|   | 1 | 000 | (00) | S |
|   |   | 200 | (20) | D G I |
|   |   | 220 | (20) | D G I |
|   |   |   | (21) | DFGH KL |
|   |   |   | (22) | S D GHI L N |

TABLE 15-5

STATES OF THE $f^5$ CONFIGURATION

| N | 2S+1 | R7 | G2 | R3 |
|---|------|-----|------|------|
| 5 | 6 | 110 | (10) | F |
|   |   |     | (11) | P    H |
|   | 4 | 111 | (00) | S |
|   |   |     | (10) | F |
|   |   |     | (20) | D G I |
|   |   | 211 | (10) | F |
|   |   |     | (11) | P    H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   |     | (30) | P FGHIK M |
|   | 2 | 100 | (10) | F |
|   |   | 210 | (11) | P    H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   | 221 | (10) | F |
|   |   |     | (11) | P    H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   |     | (30) | P FGHIK M |
|   |   |     | (31) | PDFGHIKLMNO |
|   |   |     |      | F HIK |

TABLE 15-6

STATES OF THE $f^6$ CONFIGURATION.

| N | 2S+1 | R7 | G2 | R3 |
|---|---|---|---|---|
| 6 | 7 | 100 | (10) | F |
| | 5 | 111 | (00)<br>(10)<br>(20) | S<br>  F<br> D G I |
| | | 210 | (11)<br>(20)<br>(21) | P  H<br> D G I<br> DFGH KL |
| | 3 | 110 | (10)<br>(11) | •F<br>P  H |
| | | 211 | (10)<br>(11)<br>(20)<br>(21)<br>(30) |  F<br>P  H<br> D G I<br> DFGH KL<br>P FGHIK M |
| | | 221 | (10)<br>(11)<br>(20)<br>(21)<br>(30)<br>(31) |  F<br>P  H<br> D G I<br> DFGH KL<br>P FGHIK M<br>PDFGHIKLMNO<br> F HIK |
| | 1 | 000 | (00) | S |
| | | 200 | (20) | D G I |
| | | 220 | (20)<br>(21)<br>(22) |  D G I<br> DFGH KL<br>S D GHI L N |
| | | 222 | (00)<br>(10)<br>(20)<br>(30)<br>(40) | S<br>  F<br> D G I<br>P FGHIK M<br>S DFGHIKLMN Q<br>  G I L |

TABLE 15-7

STATES OF THE $f^7$ CONFIGURATION

| N | 2S+1 | R7 | G2 | R3 |
|---|------|-----|------|-----|
| 7 | 8 | 000 | (00) | S |
|   | 6 | 110 | (10) | F |
|   |   |     | (11) | P   H |
|   |   | 200 | (20) | D G I |
|   | 4 | 111 | (00) | S |
|   |   |     | (10) | F |
|   |   |     | (20) | D G I |
|   |   | 211 | (10) | F |
|   |   |     | (11) | P   H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   |     | (30) | P FGHIK M |
|   |   | 220 | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   |     | (22) | S D GHI L N |
|   | 2 | 100 | (10) | F |
|   |   | 210 | (11) | P   H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   | 221 | (10) | F |
|   |   |     | (11) | P   H |
|   |   |     | (20) | D G I |
|   |   |     | (21) | DFGH KL |
|   |   |     | (30) | P FGHIK M |
|   |   |     | (31) | PDFGHIKLMNO F HIK |
|   |   | 222 | (00) | S |
|   |   |     | (10) | F |
|   |   |     | (20) | D G I |
|   |   |     | (30) | P FGHIK M |
|   |   |     | (40) | S DFGHIKLMN Q G I L |

# 16. THE CRYSTAL-FIELD HAMILTONIAN

We shall consider now the case of an atom or ion in an environment such as that of a crystal lattice.

The simplest treatment involves two basic assumptions.

The first assumption is that the electrons under consideration are localized in the central ion, so that they do not participate in the chemical bonding to the neighboring atoms or ions.

The second assumption considers the effect of the environment as creating an electrostatic potential due to a charge distribution around the central ion.

The assumption about the localization of the electrons implies that the basis functions involved in the treatment are restricted to be atomic orbitals of the central ion. Accordingly, the theory applies with greater success to the electronic states of those atoms or ions having an incomplete electronic shell which is relatively undisturbed by the environment, such as the transition-metal or rare-earth ions. The logical extension of the theory consists of including among the basis functions the atomic orbitals of the neighboring ions, but we shall not consider them at present.

The second assumption allows us to write the approximate Hamiltonian for the ion in the form

$$H = H_F + V_C \tag{16-1}$$

where $H_F$ is the Hamiltonian of the free ion, as given previously in Eq. (15-1), and the crystal potential $V_C$ is of the form

$$V_C = \sum_i^N V(r_i, \theta_i, \phi_i) \tag{16-2}$$

which is a sum of N one-electron operators, symmetric under permutations of electrons, and therefore an operator of the type F considered in Section 14.

The functional form of the one-electron function $V(r, \theta, \phi)$ may be established by classical arguments from a knowledge of the charge distribution which represents the effect

16-1

of the environment. This distribution has the symmetry of a certain point group, determined by the lattice.

The simplest assumption about the charge distribution is to consider it as a system of point charges located at the positions of the neighboring ions. Although this is a crude approximation, it may be refined to include more general charge distributions, still within the framework of the simple model under consideration.

In what follows we show how symmetry arguments may be used to the greatest advantage in the determination of the function $V(r, \theta, \phi)$.

## POTENTIAL OF A SYMMETRIC SYSTEM OF POINT CHARGES

The potential at the point with polar coordinates $(r, \theta, \phi)$ due to a point charge $q_a$ located at the point $(R_a, \Theta_a, \Phi_a)$ is

$$V_a = q_a (R_a^2 + r^2 - 2r R_a \cos \omega_a)^{-\frac{1}{2}}$$

$$= \frac{q_a}{R_a} \left(1 + \frac{r^2}{R_a^2} - 2 \frac{r}{R_a} \cos \omega_a\right)^{-\frac{1}{2}} \tag{16-3}$$

where $\omega_a$ is the angle between the unit vectors in the directions $(\Theta_a, \Phi_a)$ and $(\theta, \phi)$, so that

$$\cos \omega_a = \cos \Theta_a \cos \theta + \sin \Theta_a \sin \theta \cos (\Phi_a - \phi) \tag{16-4}$$

For $r < R_a$ the potential may be expanded as a power series in $r/R_a$

$$V_a = \frac{q_a}{R_a} \sum_{L=0}^{\infty} P_L (\cos \omega_a) \left(\frac{r}{R_a}\right)^L \tag{16-5}$$

The coefficients $P_L(\cos \omega_a)$ are the Legendre polynomials in the variable $\cos \omega_a$, and may be expressed in terms of the spherical harmonics of the variables $(\Theta_a, \Phi_a)$ and $(\theta, \phi)$ by means of the addition theorem

$$P_L (\cos \omega_a) = \frac{4\pi}{2L+1} \sum_M Y_L^M (\Theta_a, \Phi_a)^* Y_L^M (\theta, \phi) \tag{16-6}$$

A similar expression obtains for other sets of basis functions related to the $Y_L^M$ by a unitary transformation. If we choose an equivalent system of basis functions which are symmetry functions for a certain point group, the addition theorem may be expressed in the form

$$P_L(\cos \omega_a) = \frac{4\pi}{2L+1} \sum_{\alpha\gamma\mu} S_\mu^{(L\alpha\gamma)}(\Theta_a, \Phi_a)^* \; S_\mu^{(L\alpha\gamma)}(\theta, \phi) \qquad (16\text{-}7)$$

where the $S_\mu^{(L\alpha\gamma)}$ are the symmetry functions considered in Section 7. The index $\gamma$ runs over all the irreducible representations $\Gamma$ contained in the (reducible) representation afforded by the $Y_L^M$ for the given value of $L$. If the representation $\Gamma$ is contained $n_\gamma$ times, the index $\alpha$ assumes $n_\gamma$ different values.

Consider next a system of $\underline{n}$ identical point charges, $q_a = q$, $(a = 1, 2, \ldots, n)$, distributed about the origin according to the symmetry of a given point group, so that $R_a = R$.

Under the symmetry operations $R$, a typical point charge with coordinates $(R, \Theta_a, \Phi_a)$ will transform at least once into any other of the set. In those particular cases where the charges are located on certain elements of symmetry such as axes, planes, etc., there will be a certain number, $h_0$, of operations which leave a typical point invariant. These operations form a subgroup, and we shall have

$$n\, h_0 = h \qquad (16\text{-}8)$$

where $\underline{h}$ is the number of operations of the group.

The potential due to such a system of point charges may be written as

$$V = \frac{1}{h_0} \sum_R R\, V_a = \frac{n}{h} \sum_R R\, V_a \qquad (16\text{-}9)$$

This may also be expressed as follows

$$V = n\, P^{(A_1)}\, V_a \qquad (16\text{-}10)$$

where

$$P^{(A_1)} = \frac{1}{h} \sum_R R \qquad (16\text{-}11)$$

is the projection operator for the totally symmetric representation, $A_1$, of the group. When

16-3

this operates on the coefficients $P_L(\cos \omega_a)$ expressed in the form of Eq. (16-7), only the totally symmetric terms survive

$$\mathbb{P}^{(A_1)} \, P_L \, (\cos \omega_a) = \frac{4\pi}{2L+1} \, \sum_{\alpha} \, S^{(L\alpha A_1)}(\Theta_a, \Phi_a)^* \, S^{(L\alpha A_1)}(\theta, \phi) \qquad (16\text{-}12)$$

The expression for the potential due to one set of $\underline{n}$ equivalent point charges $\underline{q}$, takes the form

$$V(r, \theta, \phi) = \frac{nq}{R} \sum_{L=0}^{\infty} \left(\frac{r}{R}\right)^L \, \frac{4\pi}{2L+1} \, \sum_{\alpha} S^{(L\alpha A_1)}(\Theta_a, \Phi_a)^* \, S^{(L\alpha A_1)}(\theta, \phi) \qquad (16\text{-}13)$$

In the case of a crystal lattice, it is often necessary to consider more than one set of identical charges, and we shall need to assign an index $\underline{s}$, which labels the different sets, to the pertinent variables in Eq. (16-13). The total potential is obtained by adding over all the sets $\underline{s}$ of identical point charges. The final expression obtained may be written in the form

$$V(r, \theta, \phi) = \sum_{L=0}^{\infty} r^L \, \sum_{\alpha} \, \mathcal{Q}^{(L\alpha)} \, \delta^{(L\alpha)}(\theta, \phi) \qquad (16\text{-}14)$$

In this expression the $\delta^{(L\alpha)}$ functions are defined as

$$\delta^{(L\alpha)} = \sqrt{\frac{4\pi}{2L+1}} \, S^{(L\alpha A_1)} \qquad (16\text{-}15)$$

and therefore are related to the $c_Q^{(K)}$ operators in the same way that the $S^{(L\alpha A_1)}$ are related to the spherical harmonics. The index $A_1$ has been suppressed with the understanding that the $\delta^{(L\alpha)}$ are the totally symmetric functions.

The coefficents $\mathcal{Q}^{(L\alpha)}$ are lattice sums extending over all sets of equivalent point charges

$$\mathcal{Q}^{(L\alpha)} = \sum_{s} \mathcal{Q}_s^{(L\alpha)} = \sum_{s} \frac{n_s \, q_s}{R_s^{L+1}} \, \delta^{(L\alpha)}(\Theta_{sa}, \Phi_{sa})^* \qquad (16\text{-}16)$$

where the variables $\Theta_{sa}$, $\Phi_{sa}$, are the polar coordinates of an arbitrary point charge $\underline{a}$ of the equivalent set $\underline{s}$.

In the case of a continuous charge distribution the summation in Eq. (16-17) is replaced by the corresponding integral. It may be remarked that this does not change the form of the

expansion for the potential given by Eq. (16-14), but only the values of the coefficients $a^{(L,\alpha)}$.

As an example, the contributions $a_s^{(L)}$ to the coefficients in the expansion of the potential in cubic symmetry are given in Table 16-1 for the most common sets of equivalent point charges usually considered and $L \leq 6$. The totally symmetric functions are

$$S^{(0)} = Y_0^0$$

$$S^{(4)} = \frac{1}{\sqrt{24}} \left[ \sqrt{14}\, Y_4^0 + \sqrt{5}\, (Y_4^4 + Y_4^{-4}) \right] \qquad (16\text{-}17)$$

$$S^{(6)} = \frac{1}{4} \left[ \sqrt{2}\, Y_6^0 - \sqrt{7}\, (Y_6^4 + Y_6^{-4}) \right]$$

## TABLE 16-1

*POTENTIALS FOR EQUIVALENT SETS OF POINT CHARGES· CUBIC GROUP O*

| n | 6 | 12 | 8 |
|---|---|---|---|
| $(x, y, z)$ | $(0, 0, a)$ | $(a, 0, a)$ | $(a, a, a)$ |
| $R$ | $a$ | $\sqrt{2}\,a$ | $\sqrt{3}\,a$ |
| $\Phi$ | $0$ | $0$ | $\pi/4$ |
| $\sin\theta$ | $0$ | $\sqrt{1/2}$ | $\sqrt{2/3}$ |
| $\cos\theta$ | $1$ | $\sqrt{1/2}$ | $\sqrt{1/3}$ |
| $\sqrt{\dfrac{4\pi}{9}}\;Y_4^0$ | $1$ | $-\dfrac{13}{32}$ | $-\dfrac{7}{18}$ |
| $\sqrt{\dfrac{4\pi}{9}}\;(Y_4^4 + Y_4^{-4})$ | $0$ | $\dfrac{\sqrt{70}}{32}$ | $-\dfrac{\sqrt{70}}{18}$ |
| $\sqrt{\dfrac{4\pi}{9}}\;[Y_4^0 + \sqrt{\dfrac{5}{14}}\,(Y_4^4 + Y_4^{-4})]$ | $1$ | $-\dfrac{1}{4}$ | $-\dfrac{2}{3}$ |
| $\sqrt{\dfrac{4\pi}{13}}\;Y_6^0$ | $1$ | $-\dfrac{19}{128}$ | $\dfrac{2}{9}$ |
| $\sqrt{\dfrac{4\pi}{13}}\;(Y_6^4 + Y_6^{-4})$ | $0$ | $\dfrac{27\sqrt{14}}{128}$ | $-\dfrac{2\sqrt{14}}{9}$ |
| $\sqrt{\dfrac{4\pi}{13}}\;[Y_6^0 - \sqrt{\dfrac{7}{2}}\,(Y_6^4 + Y_6^{-4})]$ | $1$ | $-\dfrac{13}{8}$ | $\dfrac{16}{9}$ |
| $q_s^{(0)}$ | $6\,\dfrac{e}{a}$ | $6\sqrt{2}\,\dfrac{e}{a}$ | $\dfrac{8\sqrt{3}}{3}\,\dfrac{e}{a}$ |
| $q_s^{(4)}$ | $\sqrt{21}\,\dfrac{e}{a^5}$ | $-\dfrac{\sqrt{42}}{16}\,\dfrac{e}{a^5}$ | $-\dfrac{8\sqrt{7}}{81}\,\dfrac{e}{a^5}$ |
| $q_s^{(6)}$ | $\dfrac{\sqrt{6}}{2}\,\dfrac{e}{a^7}$ | $-\dfrac{39}{64}\,\dfrac{e}{a^7}$ | $\dfrac{32\sqrt{6}}{729}\,\dfrac{e}{a^7}$ |

The energy corresponding to the crystal field term $V_C$ is found to be very often of a magnitude comparable to the energy separation between states of the free ion. This implies that the crystal field term may not be treated as a small perturbation of the free ion Hamiltonian. It is usually necessary to determine all the matrix elements of $V_C$ between the basis functions considered in a particular problem, and solve the secular determinant corresponding to the Hamiltonian matrix.

This offers no great difficulties for the simplest electronic configurations, but as the number of electrons increases the number of basis functions increases very rapidly. As an example, the numbers of basis functions for the $d^N$ configurations are indicated in Table 16-2.

TABLE 16-2

$d^N$ *CONFIGURATIONS · NUMBER OF BASIS FUNCTIONS*

| N | Without spin | | With spin | |
|---|---|---|---|---|
| | L-states | $LM_L$-functions | J-states | JM-functions |
| 1 | 1 | 5 | 2 | 10 |
| 2 | 5 | 25 | 9 | 45 |
| 3 | 8 | 50 | 19 | 120 |
| 4 | 16 | 100 | 34 | 210 |
| 5 | 16 | 100 | 37 | 252 |

Configurations with several electrons are of no less importance than the simplest ones. Thus, for example, the states of the $Fe^{+++}$ ion belong to the $d^5$ configuration and those of $Fe^{++}$ to $d^6$ ($d^4$ hole configuration). However, in general not all the electronic states are of interest, and some of them have not even been observed experimentally in the free ions.

In view of the considerable amount of work involved in the several-electron case, it is important to consider carefully the computational scheme to be used. In order to simplify the treatment it is convenient to take advantage of symmetry considerations to the largest possible extent.

The main steps to be followed may be briefly described as follows:

a) Selection of a set of one-electron basis functions which is complete to the approximation desired.

b) Formation of all possible products of N one-electron functions.

c) Antisymetrization with respect to permutations of electron indices.

d) Construction of linear combinations of product functions which belong to the different irreducible representations of the symmetry group of the Hamiltonian.

e) Computation of the matrix elements of the Hamiltonian operator between symmetry functions.

f) Calculation of eigenvalues by solving the secular determinant corresponding to the Hamiltonian matrix, and determination of the eigenfunctions.

g) Calculation of the matrix elements of other operators of interest, transition probabilities, etc.

This only represents an outline of the different processes involved, but it is not meant to imply that the order in which they are listed is the most convenient in practice. The most difficult step is the determination of the matrix elements of all the operators involved in the expression for the Hamiltonian and it is therefore of prime importance to perform this in the simplest scheme possible.

If one considers the Hamiltonian of an ion in a crystal lattice, the terms in $H_F$, corresponding to the free ion energy, are spherically symmetric, while the crystal field term $V_C$ has the lower symmetry of one of the point groups. It is evident that the matrix elements of $H_F$ are most conveniently determined in a set of spherical basis functions. Although the term $V_C$ is not spherically symmetric, it may be expressed as a sum of terms each with different but definite transformation properties under rotations. This is simply accomplished when the functions $\delta^{(L a)}$ are expressed in terms of spherical harmonics. The matrix elements of the different terms in this sum may be obtained without great difficulties in spherical basis. In fact, if the reduced matrix elements are known, the application of the Wigner-Eckart theorem in spherical basis is straightforward.

If this scheme is followed, the transformation of the Hamiltonian to the basis appropriate to the point group of $V_C$ may be accomplished by a similarity transformation. The transformation between spherical basis functions and the symmetry functions of a given point group is rather simple, as it is diagonal in all the quantum numbers except M, and the matrix elements depend only on J, M, and the particular point group in question. Moreover, this transformation may be determined once and for all, and the results have been given in Section 7.

According to this procedure, the problem is actually broken-up into two parts, one of which is independent of the lattice symmetry, the other independent of electronic configuration, number of electrons, etc., but only on the values of J for the different states.

By exactly the same type of reasoning one easily finds the advantages of classifying the basis functions for configurations of equivalent electrons according to those groups of symmetry such as $R_5$, or $R_7$ and $G_2$, previously introduced. Although the Hamiltonian is not totally symmetric under those groups, it may be expressed as a sum of terms which belong to irreducible representations of these groups. Thus, for example the set of fourteen operators

$$U_q^{(2)} \sim \sum_i Y_q^{(2)}(i) \qquad -2 \le q \le 2$$

$$U_q^{(4)} \sim \sum_i Y_q^{(4)}(i) \qquad -4 \le q \le 2$$

(16-18)

all together form a basis for the irreducible representation (20) of the group $R_5$. Therefore, in a set of basis functions classified according to the irreducible representations of $R_5$, there are many matrix elements for these operators which vanish on account of symmetry. Thus, for example, for the $d^5$ configuration, the matrices of the corresponding crystal field operators $\sum_i Y_q^{(2)}(i)$ and $\sum_i Y_q^{(4)}(i)$ have the form



(16-19)

where the unshaded areas correspond to the matrix elements which vanish for symmetry reasons.

In view of these considerations, we have determined the angular factor of the reduced matrix elements of the operators which appear in the expression of the crystal potential for configurations of $p^N$, $d^N$, and $f^N$ electrons in the gSL scheme, and these are listed in the Tables. These do not include the results for the $^2L$ states of $f^5$ and $f^7$, nor the $^3L$ and $^1L$ states of $f^6$. From these, the angular factors of the reduced matrix elements for states of

16-9

the mixed configurations may be obtained by simple coupling formulae given in Section 12.

The reduced matrix elements are given for the operators $C_Q^{(K)}$ which differ from the corresponding operators for the spherical harmonics by inclusion of the factor $(4\pi/2K + 1)^{1/2}$

$$C_Q^{(K)} = \left(\frac{4\pi}{2K + 1}\right)^{1/2} \sum_i^N Y_Q^{(K)} (\theta_i, \phi_i) \tag{16-20}$$

These are related to the $U_Q^{(K)}$ operators of Eq. (15-7) by the relation

$$C_Q^{(K)} = (\ell \| c^{(K)} \| \ell) U_Q^{(K)} \tag{16-21}$$

where

$$(\ell \| c^{(K)} \| \ell) = (-1)^{\ell} (2\ell + 1) \begin{pmatrix} \ell & K & \ell \\ 0 & 0 & 0 \end{pmatrix} \tag{16-22}$$

For K odd, the $C_Q^{(K)}$ operators have vanishing matrix elements between states of the configurations of equivalent electrons, since the reduced matrix elements of the corresponding one-electron operators $c_Q^{(K)}$ vanish according to Eq. (16-22). However, the reduced matrix elements of the $U_Q^{(K)}$ operators do not vanish and these are given in the Tables. The sign of the reduced matrix elements of these operators determines the choice of phases for the states.

The states are classified according to gSL, as this is the best choice for the general case. If the spin-orbit coupling is to be treated rigorously it is convenient to operate in the $|\alpha J M)$ basis. In this case the reduced matrix elements may be easily obtained from those listed by means of the coupling formulae of Section 12, in particular Eq. (12-16). The 6-j symbols which appear in these formulae have not been tabulated on account of their large number. In our scheme of calculations the needed 6-j symbols are computed by use of a program for the IBM electronic computer.

# LIST OF REFERENCES

1. E. P. Wigner, "Group Theory and its Application to the Quantum Mechanics of Atomic Spectra", Academic Press, New York and London, 1959.

2. A. R. Edmonds, "Angular Momentum in Quantum Mechanics", Princeton University Press, 1957.

3. M. E. Rose, "Elementary Theory of Angular Momentum", John Wiley and Sons, New York, 1957.

4. H. Weyl, "The Theory of Groups and Quantum Mechanics", Dover Publications, New York, 1949.

5. H. A. Bethe, Ann. Physik, **3**, 133 (1929).

6. W. Opechowski, Physica, **7**, 552 (1940).

7. G. F. Koster, Phys. Rev. **109**, 227 (1958).

8. G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943); **76**, 1352 (1949).

9. E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra", Cambridge Univ. Press, 1957.

10. N. M. Gray and L. A. Wills, Phys. Rev. **38**, 248 (1931).

11. H. A. Jahn, Proc. Roy. Soc. (London) **201A**, 516 (1950).

12. B. H. Flowers, Proc. Roy. Soc. (London) **210A**, 497 (1951).

# APPENDIX A

## LEGENDRE POLYNOMIALS (UNNORMALIZED)

*Definition:*

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2-1)^\ell \qquad\qquad (A-1)$$

*General expression:*

$$P_\ell(x) = \frac{1 \cdot 3 \cdot 5 \cdots (2\ell-1)}{\ell!} \left[ x^\ell - \frac{\ell(\ell-1)}{2(2\ell-1)} x^{\ell-2} \right.$$

$$+ \frac{\ell(\ell-1)(\ell-2)(\ell-3)}{2 \cdot 4 \cdot (2\ell-1)(2\ell-3)} x^{\ell-4} \qquad\qquad (A-2)$$

$$\left. - \frac{\ell(\ell-1)(\ell-2)(\ell-3)(\ell-4)(\ell-5)}{2 \cdot 4 \cdot 6 \cdot (2\ell-1)(2\ell-3)(2\ell-5)} x^{\ell-6} + \ldots \right]$$

### TABLE A-1
### *LEGENDRE POLYNOMIALS*

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1)$$

$$P_3(x) = \frac{1}{2}(5x^3 - 3x)$$

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5(x) = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

$$P_6(x) = \frac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5)$$

$$P_7(x) = \frac{1}{16}(429x^7 - 693x^5 + 315x^3 - 35x)$$

$$P_8(x) = \frac{1}{128}(6435x^8 - 12012x^6 + 6930x^4 - 1260x^2 + 35)$$

Another convenient form in terms of the cosines of the angles $n\theta$, is

$$P_\ell(\cos\theta) = \frac{1\cdot3\cdot5\cdot\quad(2\ell-1)}{2\cdot4\cdot6\cdot\quad\cdot2\ell}\,[\,2\cos\ell\,\theta\,+$$

$$+\,2\,\frac{1\cdot\ell}{1\cdot(2\ell-1)}\cos(\ell-2)\,\theta + 2\,\frac{1\cdot3\cdot\ell(\ell-1)}{1\cdot2\cdot(2\ell-1)(2\ell-3)}\cos(\ell-4)\,\theta \qquad (A\text{-}3)$$

$$+\,2\,\frac{1\cdot3\cdot5}{1\cdot2\cdot3}\quad\frac{\ell(\ell-1)(\ell-2)}{(2\ell-1)(2\ell-3)(2\ell-5)}\cos(\ell-6)\,\theta + \dots\,]$$

### TABLE A-2
#### LEGENDRE POLYNOMIALS

$P_0(\cos\theta) = 1$

$P_1(\cos\theta) = \cos\theta$

$P_2(\cos\theta) = \frac{1}{4}(3\cos2\theta + 1)$

$P_3(\cos\theta) = \frac{1}{8}(5\cos3\theta + 3\cos\theta)$

$P_4(\cos\theta) = \frac{1}{64}(35\cos4\theta + 20\cos2\theta + 9)$

$P_5(\cos\theta) = \frac{1}{128}(63\cos5\theta + 35\cos3\theta + 30\cos\theta)$

$P_6(\cos\theta) = \frac{1}{512}(231\cos6\theta + 126\cos4\theta + 105\cos2\theta + 50)$

$P_7(\cos\theta) = \frac{1}{1024}(429\cos7\theta + 231\cos5\theta + 189\cos3\theta + 175\cos\theta)$

$P_8(\cos\theta) = \frac{1}{16384}(6435\cos8\theta + 3432\cos6\theta + 2772\cos4\theta + 2520\cos2\theta + 1225)$

## NORMALIZED ASSOCIATED LEGENDRE POLYNOMIALS

*Definition:*

$$\Theta_\ell^m(x) = \frac{(-1)^m}{2^\ell\cdot\ell!}\sqrt{\frac{2\ell+1}{2}\,\frac{(\ell-m)!}{(\ell+m)!}}\,(1-x^2)^{\frac{m}{2}}(\tfrac{d}{dx})^{\ell+m}(x^2-1)^\ell \qquad (A\text{-}4)$$

$\ell$ and m are integers and $0 < m \leq \ell$. The expression also has a meaning for negative m, but $\Theta_\ell^m(x)$ and $\Theta_\ell^{-m}(x)$ are not independent.

A-2

$$\Theta_\ell^{-m}(x) = (-1)^m \ \Theta_\ell^m(x) \tag{A-5}$$

The $\Theta_\ell^m$ are single-valued, continuous, and quadratically integrable in the interval $-1 < x < 1$.

*Orthogonality:*

$$\int_{-1}^1 \Theta_\ell^m(x) \ \Theta_{\ell'}^m(x) \, dx = \delta_{\ell \ell'} \tag{A-6}$$

*Other properties:*

The $\Theta_\ell^m(x)$ are real functions.

$$\Theta_\ell^m(-x) = (-1)^{\ell + m} \ \Theta_\ell^m(x)$$
$$= (-1)^\ell \ \Theta_\ell^{-m}(x) \tag{A-7}$$

*General expression:* (for $x = \cos\theta$)

$$\Theta_\ell^m = (-\sin\theta)^m \ \frac{(2\ell)!}{2^\ell \ \ell! \ (\ell - m)!} \ \sqrt{\frac{2\ell+1}{2} \cdot \frac{(\ell-m)!}{(\ell+m)!}} \ [ \ (\cos\theta)^{\ell-m}$$

$$- \frac{(\ell-m)(\ell-m-1)}{2(2\ell-1)} \ (\cos\theta)^{\ell-m-2} \tag{A-8}$$

$$+ \frac{(\ell-m)(\ell-m-1)(\ell-m-2)(\ell-m-3)}{2 \cdot 4 \cdot (2\ell-1)(2\ell-3)} (\cos\theta)^{\ell-m-4} - \ .... \ ]$$

## SPHERICAL HARMONICS

*Definition:*

$$Y_\ell^m(\theta,\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \ \Theta_\ell^m(\cos\theta) \tag{A-9}$$

$\ell$ and m are integers, and $-\ell < m < \ell$. There are $2\ell + 1$ independent functions for a given value of $\ell$.

$$Y_\ell^m(\theta,\phi)^* = (-1)^m \ Y_\ell^{-m}(\theta,\phi) \tag{A-10}$$

*Orthonormality:*

$$\int_0^{2\pi} d\phi \int_0^\pi Y_\ell^m(\theta,\phi)^* \ Y_{\ell'}^{m'}(\theta,\phi) \sin\theta \, d\theta = \delta_{\ell\ell'} \ \delta_{mm'} \tag{A-11}$$

A-3

*Addition Theorem:*

$$P_\ell (\cos \theta) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^m (\theta_1, \phi_1)^* \, Y^m (\theta_2, \phi_2) \tag{A-12}$$

where $\theta$ is the angle between the unit vectors in the directions $(\theta_1, \phi_1)$ and $(\theta_2, \phi_2)$. $P_\ell(\cos \theta)$ is the unnormalized Legendre polynomial of degree $\ell$. For $x = \cos \theta$,

$$P_\ell(x) = \sqrt{\frac{2}{2\ell+1}} \; \Theta_\ell^0(x) = \sqrt{\frac{4\pi}{2\ell+1}} \; Y_\ell^0 (\theta, 0) \tag{A-13}$$

TABLE A-3

*SPHERICAL HARMONICS*

$$\boxed{Y_\ell^{-m} = (-1)^m (Y_\ell^m)^*}$$

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^1 = -\frac{1}{2} \sqrt{\frac{3}{4\pi} \cdot 2} \; \sin \theta \cdot e^{i\phi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_2^2 = \frac{1}{4} \sqrt{\frac{5}{4\pi} \cdot 2 \cdot 3} \cdot \sin^2 \theta \cdot e^{i2\phi}$$

$$Y_2^1 = -\frac{1}{2} \sqrt{\frac{5}{4\pi} \cdot 2 \cdot 3} \; \sin \theta \cdot \cos \theta \cdot e^{i\phi}$$

$$Y_2^0 = \frac{1}{2} \sqrt{\frac{5}{4\pi}} (3 \cos^2 \theta - 1)$$

$$Y_3^3 = -\frac{1}{4} \sqrt{\frac{7}{4\pi} \cdot 5} \cdot \sin^3 \theta \cdot e^{i3\phi}$$

$$Y_3^2 = \frac{1}{4} \sqrt{\frac{7}{4\pi} \cdot 2 \cdot 3 \cdot 5} \; \sin^2 \theta \cdot \cos \theta \cdot e^{i2\phi}$$

$$Y_3^1 = -\frac{1}{4} \sqrt{\frac{7}{4\pi} \cdot 3} \cdot \sin \theta \, (5 \cos^2 \theta - 1) \cdot e^{i\phi}$$

$$Y_3^0 = \frac{1}{2} \sqrt{\frac{7}{4\pi}} (5 \cos^3 \theta - 3 \cos \theta)$$

## SPHERICAL HARMONICS
### (Continued)

$$Y_4^4 = \frac{1}{16} \sqrt{\frac{9}{4\pi} \cdot 2 \cdot 5 \cdot 7} \sin^4 \theta \cdot e^{i4\phi}$$

$$Y_4^3 = -\frac{1}{4} \sqrt{\frac{9}{4\pi} \cdot 5 \cdot 7} \sin^3 \theta \cdot \cos \theta \cdot e^{i3\phi}$$

$$Y_4^2 = \frac{1}{8} \sqrt{\frac{9}{4\pi} \cdot 2 \cdot 5} \cdot \sin^2 \theta \cdot (7 \cos^2 \theta - 1) \cdot e^{i2\phi}$$

$$Y_4^1 = -\frac{1}{4} \sqrt{\frac{9}{4\pi} \cdot 5} \cdot \sin \theta \cdot (7 \cos^3 \theta - 3 \cos \theta) \cdot e^{i\phi}$$

$$Y_4^0 = \frac{1}{8} \sqrt{\frac{9}{4\pi}} (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$$

$$Y_5^5 = -\frac{3}{16} \sqrt{\frac{11}{4\pi} \cdot 7} \cdot \sin^5 \theta \cdot e^{i5\phi}$$

$$Y_5^4 = \frac{3}{16} \sqrt{\frac{11}{4\pi} \cdot 2 \cdot 5 \cdot 7} \sin^4 \theta \cdot \cos \theta \cdot e^{i4\phi}$$

$$Y_5^3 = -\frac{1}{16} \sqrt{\frac{11}{4\pi} \cdot 5 \cdot 7} \sin^3 \theta (9 \cos^2 \theta - 1) \cdot e^{i3\phi}$$

$$Y_5^2 = \frac{1}{8} \sqrt{\frac{11}{4\pi} \cdot 2 \cdot 3 \cdot 5 \cdot 7} \sin^2 \theta \cdot (3 \cos^3 \theta - \cos \theta) \cdot e^{i2\phi}$$

$$Y_5^1 = -\frac{1}{16} \sqrt{\frac{11}{4\pi} \cdot 2 \cdot 3 \cdot 5} \sin \theta (21 \cos^4 \theta - 14 \cos^2 \theta + 1) \cdot e^{i\phi}$$

$$Y_5^0 = \frac{1}{8} \sqrt{\frac{11}{4\pi}} (63 \cos^5 \theta - 70 \cos^3 \theta + 15 \cos \theta)$$

$$Y_6^6 = \frac{1}{32} \sqrt{\frac{13}{4\pi} \cdot 3 \cdot 7 \cdot 11} \sin^6 \theta \cdot e^{i6\phi}$$

$$Y_6^5 = -\frac{3}{16} \sqrt{\frac{13}{4\pi} \cdot 7 \cdot 11} \sin^5 \theta \cdot \cos \theta \cdot e^{i5\phi}$$

$$Y_6^4 = \frac{3}{32} \sqrt{\frac{13}{4\pi} \cdot 2 \cdot 7} \sin^4 \theta (11 \cos^2 \theta - 1) \cdot e^{i4\phi}$$

$$Y_6^3 = -\frac{1}{16} \sqrt{\frac{13}{4\pi} \cdot 3 \cdot 5 \cdot 7} \sin^3 \theta (11 \cos^3 \theta - 3 \cos \theta) \cdot e^{i3\phi}$$

$$Y_6^2 = \frac{1}{32} \sqrt{\frac{13}{4\pi} \cdot 3 \cdot 5 \cdot 7} \sin^2 \theta (33 \cos^4 \theta - 18 \cos^2 \theta + 1) \cdot e^{i2\phi}$$

## TABLE A-3

### SPHERICAL HARMONICS
### (Continued)

$$Y_6^1 = -\frac{1}{16} \sqrt{\frac{13}{4\pi}} \, 2 \cdot 3 \cdot 7 \sin \theta \, (33 \cos^5 \theta - 30 \cos^3 \theta + 5 \cos \theta) \cdot e^{i\phi}$$

$$Y_6^0 = \frac{1}{16} \sqrt{\frac{13}{4\pi}} (3 \cdot 7 \cdot 11 \cdot \cos^6 \theta - 5 \cdot 7 \cdot \cos^4 \theta + 3 \cdot 5 \cdot 7 \cos^2 \theta - 5)$$

To obtain expression in cartesian coordinates, use the relations:

$$\cos \theta = \frac{z}{r} , \qquad \sin^m \theta \cdot e^{\pm im\phi} = \left(\frac{x \pm iy}{r}\right)^m \qquad (A\text{-}14)$$